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### (54) HYDROGEN STORAGE ALLOY EXCELLENT IN DURABILITY AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a hydrogen storage alloy having high hydrogen occluding capacity and a long term repeated hydrogen absorbing and releasing service life (being hard to be pulverized) suitable for storing and transporting hydrogen or the like, usable at a temp. in the vicinity of a room temp., excellent in oxidation-resistance and easily treatable in the air and to provide a method for producing the same.

SOLUTION: A hydrogen storage alloy having a compsn. expressed by  $Ti_aV_{1-a-b-c-d}Cr_bAcB_d$  (A denotes one or more kinds among Mn, Fe, Co, Cu, Nb, Zn, Zr, Mo, Ag, Hf, Ta, W, Al, Si, C, N, P and B, B denotes one or more kinds among Ln (lanthanoid series metals) and Y,  $a=0.2$  to  $0.5$ ,  $b=0.1$  to  $0.4$ ,  $c=0.01$  to  $0.2$  and  $d=0.001$  to  $0.03$ ) and in which the average grain size of the main phases is regulated to  $40\ \mu m$  is produced by a rapid solidifying method.] The surface of this hydrogen storage alloy is applied with Ni coating, then, heat treatment is executed at  $400$  to  $1,000^\circ C$ , or the surface of the hydrogen storage alloy is applied with Ni coating by a mechanical alloying method to form an Ni-added layer essentially consisting of a Ti-Ni compd., by which its oxidation resistance remarkably improves.

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(54) 【発明の名称】 耐久性に優れる水素吸蔵合金とその製造方法

(57) 【要約】

【課題】 水素の貯蔵・輸送用等に適した、高い水素吸蔵能力と長期繰り返し水素吸収・放出寿命（微粉化しにくい）とをもち、室温近傍の温度で使用でき、かつ耐酸化性に優れ、大気中で容易に取扱うことができる水素吸蔵合金とその製造方法を提供する。

【解決手段】  $Ti_a V_{1-a-b-c-d} Cr_b A_c B_d$ （式中、Aは、Mn、Fe、Co、Cu、Nb、Zn、Zr、Mo、Ag、Hf、Ta、W、Al、Si、C、N、P、Bの1種以上；BはLn（ランタノイド系金属）およびYの1種以上； $a = 0.2 \sim 0.5$  以下、 $b = 0.1 \sim 0.4$ 、 $c = 0.01 \sim 0.2$ 、 $d = 0.001 \sim 0.03$ ）で表される組成を持ち、主相の平均結晶粒径が40  $\mu m$ 以下である水素吸蔵合金を急冷凝固法で製造する。この水素吸蔵合金の表面をNi被覆し、次いで400～750℃の温度で熱処理を行うか、または水素吸蔵合金の表面をメカニカルアロイング法によりNi被覆して、表面にTi-Ni化合物を主体とするNi付加層を形成すると、耐酸化性が著しく向上する。

## 【特許請求の範囲】

【請求項 1】 式： $Ti_a V_{1-a-b-c-d} Cr_b A_c B_d \cdots \textcircled{1}$

で示される組成を持ち、主相の平均結晶粒径が $40\mu m$ 以下であることを特徴とする水素吸蔵合金。上記式中、Aは、Mn、Fe、Co、Cu、Nb、Zr、Mo、Ag、Hf、Ta、W、Al、Si、C、N、P、およびBから選ばれた1種または2種以上の元素を意味し、

BはLn（ランタノイド系金属）およびYから選ばれた1種または2種以上の元素を意味し、

aの値は0.2以上、0.5以下、

bの値は0.1以上、0.4以下、

cの値は0.01以上、0.2以下、

dの値は0.001以上、0.03以下。

【請求項 2】 表面にTi-Ni化合物を主体とするNi付加層を有する、請求項 1 記載の水素吸蔵合金。

【請求項 3】  $\textcircled{1}$ 式で示される組成を持つ合金を急冷凝固法により製造することを特徴とする、請求項 1 記載の水素吸蔵合金の製造方法。

【請求項 4】  $\textcircled{1}$ 式で示される組成を持つ合金を急冷凝固法により製造し、この水素吸蔵合金の表面をNiで被覆し、次いで $400\sim 1000^\circ C$ の温度で熱処理を行うことを特徴とする、請求項 2 記載の水素吸蔵合金の製造方法。

【請求項 5】  $\textcircled{1}$ 式で示される組成を持つ合金を急冷凝固法により製造し、この水素吸蔵合金の表面をメカニカルアロイング法によりNiで被覆することからなる、請求項 2 記載の水素吸蔵合金の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、水素吸収量（水素吸蔵能力）が高く、同時に繰り返し水素吸収放出による特性劣化が少なく、室温近傍の温度で利用可能で、比較的安価といった特徴を持つ、耐久性に優れた水素吸蔵合金とその製造方法に関する。これらの特徴を持つ本発明の水素吸蔵合金は、特に水素ガス貯蔵・輸送用、水素ガス分離・精製用、さらには熱輸送システムや冷却システム、静的コンプレッサーなどに最適である。

## 【0002】

【従来の技術】水素ガスは、燃焼すると水になり、化石燃料のように炭酸ガスや硫黄酸化物を形成することがないため、クリーンなエネルギー源である。

【0003】水素ガスの貯蔵・輸送は、一般に圧縮して高圧ガスとして行われている。液体水素の貯蔵には $-253^\circ C$ の低温貯蔵容器が必要で、蒸発損失も大きい上、水素の液化に多量のエネルギーが必要であるため、窒素のように液化して貯蔵するのは困難であるからである。しかし、高圧水素ガスには重くて嵩張る耐圧容器が必要であるにもかかわらず、体積は200分の1程度にしかならず非効率である上、安全性にも問題がある。

【0004】そこで、冷却・加熱により水素ガスを可逆的に吸収・放出できる水素吸蔵合金を水素ガスの貯蔵・

輸送に利用することが検討されてきた。水素吸蔵合金は、単位体積当たりの水素ガスの貯蔵密度が高圧水素ガス容器より高く、より軽量かつ小体積の水素ガス貯蔵容器となり、水素ガスの輸送も容易になる。また、低圧であることから安全性が高く、輸送中の機械的な衝撃にも強い。

【0005】水素の貯蔵・輸送を目的とする水素吸蔵合金は従来より開発されており、小規模な水素の貯蔵には既に利用されている。また、ガソリンの代替燃料として水素ガスを利用する低公害水素自動車の研究も進んでおり、これにもFeTi系をはじめとする各種の水素吸蔵合金が水素貯蔵デバイスとして検討されている。

【0006】水素吸蔵合金の実用化が期待される用途には他に次のようなものがある。水素吸蔵合金の水素の吸収（水素化）と放出（水素化物の分解）は、熱の放出と吸収を伴う可逆反応であり、熱-化学エネルギー変換機能を持つ。この機能を利用して、熱エネルギーの貯蔵・輸送システムや化学的ヒートポンプとして冷却システムに使用することができる。

【0007】また、低温で水素ガスを吸収させた水素吸蔵合金を高温に加熱すると、高圧の水素ガスが放出される。それにより熱エネルギーを機械エネルギーに変換する機能も果たす。この機能は、熱駆動型の静的水素コンプレッサやアクチュエータとして利用できる。

【0008】水素吸蔵合金の水素ガスの吸収・放出速度は、他のガス成分の吸収・放出速度より大きく、水素同位体間でも差がある。従って、水素吸蔵合金を用いて水素または特定の水素同位体を選択的に吸収または放出させることにより、混合ガスからの高純度水素ガスの分離、不純水素ガスの精製、さらには水素同位体の分離が可能である。

【0009】このように水素吸蔵合金には幅広い用途があるが、どの用途に対しても、水素吸蔵量が最も重要な特性である。また、上記の用途はいずれも比較的多量の水素吸蔵合金を必要とするので、水素吸蔵合金を繰り返し使用しても機能低下が少なく、耐久性に優れていることと、合金の価格が比較的安価であることも重要である。用途によっては室温近傍の比較的低い温度（例、 $150^\circ C$ 以下）で水素の吸収・放出が起こることも求められる。

【0010】例えば、実用化が先行した $LaNi_5$ または $MnNi_5$ で代表される $AB_5$ 型の水素吸蔵合金は高価であるので、水素吸蔵合金の使用量が少ないNi-水素電池等の小型二次電池用には使用できても、水素ガス貯蔵用といった大量の水素吸蔵合金が必要な用途には、価格面から使用が困難である。また、水素吸蔵量もそれほど多くない。

【0011】特公昭59-38293号公報には、比較的安価

で水素吸蔵量の多い水素吸蔵合金としてTi-Cr-V系合金が記載されている。合金の製造方法としてはアーク法しか具体的に説明されていない。特開平 7-252560号公報にも同様な成分で構成される水素吸蔵合金が記載されている。特開平 7-268513号公報と特開平 7-268514号公報には、Ti-V-Ni系の類似の水素吸蔵合金が記載されている。

【0012】また、特開昭60-190570号公報には、水素吸蔵合金粉末に湿式無電解メッキにより銅および/またはニッケル金属を被覆することで、雰囲気中の不純物ガスによる汚染の影響を小さくでき、初期活性化が不要ないし軽減できることが説明されている。

【0013】

【発明が解決しようとする課題】水素吸蔵合金の水素ガスの吸収と放出は、それぞれ体積の膨張と収縮を伴う化学反応である。実用的な反応速度を得るには、水素吸蔵合金を粉末状で使用して表面積を増大させる必要がある。しかし、使用中に合金粉末の体積の膨張と収縮が繰り返されると、内部歪みにより粉末に亀裂が入り、やがて細かな粒子に割れて粉末が微粉化する。微粉化が進行すると、閉塞により水素ガスが容易に流れなくなったり、微粉が水素ガスの流れに混じってガス配管内に移動する。従って、この微粉化が水素吸蔵合金の長期繰り返し水素吸収・放出寿命（即ち、耐久性）低下の大きな原因となる。

【0014】前述したTi-Cr-V系水素吸蔵合金およびTi-V-Ni系合金は、水素吸蔵量の多い合金として開発されたものであるが、実際には所定の水素吸蔵量に達しないことが多く、上記の微粉化による耐久性の問題も解決できていない。

【0015】例えば、特公昭59-38293号公報に記載のTi-Cr-V系水素吸蔵合金は、この公報に記載されているようにアーク法で製造すると、凝固速度が遅いため、第2相として、水素吸蔵量の低いTiCr<sub>2</sub>金属間化合物がかなりの割合で析出し、水素吸蔵量が低下する。また、水素吸収・放出の繰り返し中にこの第2相を起点として合金粉末に亀裂が入り、微粉化が促進されるという問題点もある。

【0016】特開平 7-252560号公報に記載の水素吸蔵合金は、その実施例では、上記の第2相を減らすため、1200~1400℃という高温で保持して立方晶の単相組織とした後、直ちに水冷により急冷する製法がとられている。しかし、この方法では、高温加熱保持の際に結晶粒の粗大化が生じるため、第2相の析出量は減少しても、粗大化により材料自体の強度が弱くなり、微粉化し易くなる。その上、工業的に大量生産する際には大型インゴットを用いるため、水冷でも十分な冷却速度が得られず、Ti-Cr化合物を主体とする第2相の粗大析出物が形成され、水素吸蔵量も低下する。

【0017】特開平 7-268513号および同 7-268514号

の各公報に記載のTi-V-Ni系水素吸蔵合金は、Ti-V系合金からなる母相の粒界に、第2相のTi-Ni合金相またはAB<sub>2</sub>型ラーベス合金相が3次元網目骨格を形成した組織を持つ。この粒界相が合金の水素との反応性を向上させるため、母相に若干の酸化があっても、この粒界相を介して水素ガスの吸収・放出が可能である。しかし、水素吸蔵能力の低い第2相を3次元網目構造を形成するほど多量に析出させるため、合金全体の水素貯蔵量が低下する。また、第2相を起点とした微粉化の問題も避けられない。

【0018】水素吸蔵合金の耐酸化性も重要な特性である。水素吸蔵合金は大気中に放置されると表面が酸化され、酸化膜が形成される。特に、V含有合金は酸化膜が形成され易い。この酸化膜は水素吸収の障害となり、所定の水素吸蔵能力を発揮することができない。そのため、水素吸蔵合金粉末は、使用前に酸化膜を除去するため活性化処理が必要となることが多い。この活性化処理は、合金粉末を耐圧容器に入れ、数十Kg/cm<sup>2</sup>の高圧の水素ガスを高温で1日~数日間作用させることにより行われ、容器と処理のどちらにも費用がかかる。従って、活性化処理が不要となるように、空气中に放置しても酸化されにくい水素吸蔵合金粉末が求められている。

【0019】特開昭60-190570号公報に記載の無電解メッキによる水素吸蔵合金粉末の金属被覆は、この要請に応えたもので、水素吸蔵合金粉末の耐酸化性の向上には有効であるが、被覆金属が水素吸蔵能力を全く持たないCuやNiであるため、被覆金属の分だけ水素吸蔵量が減少する。

【0020】本発明は、水素ガスの貯蔵・輸送、水素ガスの精製・分離、熱輸送・冷却システム、水素コンプレッサーなどの用途に適用可能な、高い水素吸蔵能力を持ち、微粉化しにくく長期繰り返し水素吸収・放出寿命（耐久性）に優れ、室温近傍の比較的低い（150℃以下）の温度で使用でき、かつ大気中に放置しても水素吸蔵特性の劣化の少ない、比較的安価な水素吸蔵合金を提供することを課題とする。

【0021】

【課題を解決するための手段】本発明者らは、急冷凝固法により製造された、結晶粒径の小さいTi-Cr-V系水素吸蔵合金が、高い水素吸蔵能力と優れた繰り返し水素吸収・放出寿命（耐久性）をもち、室温近傍の比較的低温で使用できることを先に見出した。

【0022】この水素吸蔵合金はH/M（合金を構成する構成原子数に対する吸蔵された水素原子数の比）が1.5以上、最高で1.7台の高い水素吸蔵量を示すが、それでもVに代表される体心立方格子金属の理論上の最大水素吸蔵量（H/M=2）に比べるとまだ少し低く、水素吸蔵量をさらに増大させる余地が残っていた。その後の研究の結果、上記の合金組成に少量の他の元素を添加すると、水素吸蔵量がさらに増大することがわかり、本発

明に到達した。

【0023】本発明は、式： $Ti_a V_{1-a-b-c-d} Cr_b A_c B_d$  で表される組成を持ち、主相の平均結晶粒径が $40\mu m$ 以下であることを特徴とする水素吸蔵合金である。上の式において、Aは、Mn、Fe、Co、Cu、Nb、Zn、Zr、Mo、Ag、Hf、Ta、W、Al、Si、C、N、P、およびBから選ばれた1種または2種以上の元素を意味し、BはLn（ランタノイド系金属）およびYから選ばれた1種または2種以上の元素を意味し、aの値は0.2以上、0.5以下、bの値は0.1以上、0.4以下、cの値は0.01以上、0.2以下、dの値は0.001以上、0.03以下である。

【0024】この結晶粒径の小さい水素吸蔵合金は、急冷凝固法により製造することができる。本発明の好適態様においては、水素吸蔵合金が表面にTi-Ni化合物を主体とするNi付加層を有している。このNi付加層は、①急冷凝固法により製造した水素吸蔵合金の表面をNiで被覆し、次いで400~1000℃の温度で熱処理を行うか、或いは②この水素吸蔵合金の表面をメカニカルアロイング法によりNiで被覆することにより形成することができる。

【0025】

【発明の実施の形態】以下、本発明の水素吸蔵合金とその製造方法について詳しく説明する。本発明の水素吸蔵合金の特徴は、(1)  $Ti_a V_{1-a-b-c-d} Cr_b A_c B_d$  (①式、式中、A、B、a~dは上記と同じ) で示される化学組成と、(2) 主相の平均結晶粒径が $40\mu m$ 以下と微細である、という2点である。

【0026】この水素吸蔵合金の主相は体心立方晶であり、この結晶格子はTi、V、Crの3元素からなり、その一部がA元素で置換された固溶体である。上記(2)の微細な主相の平均結晶粒径は、水素吸蔵合金をロール急冷法やガスアトマイズ法といった急冷凝固法により製造することにより得られる。従って、本発明の水素吸蔵合金は、「上記①式で示される化学組成を持つ急冷凝固された合金」であるといえる。例えば、アーク溶解法のように凝固時の冷却速度が遅くなると、凝固中に結晶粒が成長して粗大になるため、主相の平均結晶粒径は $40\mu m$ を超える。

【0027】本発明の水素吸蔵合金が、高い水素吸蔵能力を持ち、微粉化しにくく耐久性に優れ、かつ室温近傍の比較的低い(150℃以下)の温度で使用できる理由は次のように推測される。

【0028】本発明者らが先に見出したように、急冷凝固した体心立方晶のTi-V-Cr系合金は、大気圧に近い0.1 MPaの水素平衡圧(水素吸収・放出反応の平衡ガス圧)を示す温度が150℃以下と低く、150℃以下の温度範囲でも、多量の水素を吸収することができ、かつ微粉化しにくいため繰り返し水素吸収・放出寿命に優れている。

【0029】しかし、この高い水素吸蔵量や優れた耐久性は、アーク溶解法のように溶解後の凝固が遅い従来の

方法で製造された合金では得られない。これは、凝固時の冷却速度が低下すると、水素吸蔵量の少ないTiCr<sub>2</sub>を主体とする第2相が、凝固中にかなりの割合で析出するためである。この第2相の析出物は、水素吸蔵量を低下させるだけでなく、水素平衡圧を低下させて吸収した水素の可逆的な放出を不可能にし、さらに粒界破壊の起点となるため、微粉化を起り易くする。換言すると、本発明の水素吸蔵合金では、この第2相の析出量が非常に少ないため、この相に起因する水素吸蔵量の低下や微粉化を避けることができる。

【0030】本発明によれば、急冷凝固されたTi-V-Cr系合金に上記①式のAおよびBで示される元素を添加することにより、元合金とほぼ温度・圧力で水素ガスを吸収・放出する特性を維持し、かつ上記第2相の形成も抑えながら、水素吸蔵量をさらに増大させることができる。その理由は完全に解明されたわけではないが、次のように考えられる。

【0031】A元素(Mn、Fe、Co、Cu、Nb、Zn、Zr、Mo、Ag、Hf、Ta、W、Al、Si、C、N、P、B)は、主相の体心立方晶を構成するTi、V、Crと置換して格子寸法を拡大することで、合金自体の水素吸蔵量を高めていると予想される。これらの元素も、溶解後の冷却速度が遅いと、TiまたはCrとの金属間化合物、炭化物、ホウ化物を形成しやすく、水素吸蔵量が低下する。従って、高い水素吸蔵量を得るには、このような化合物の晶出または析出を抑制するために、急冷凝固する必要がある。それにより、この化合物が起点となる微粉化も抑制される。

【0032】B元素(ランタノイド系金属<Ln>またはY)は、主相の体心立方晶にはほとんど存在せず、合金中に含まれる不純物酸素と酸化物を形成して存在すると考えられる。不純物酸素は主相の体心立方晶の金属原子間に侵入する状態で存在しているが、これらの元素が侵入する位置は、水素を吸蔵させた場合に水素原子が侵入する位置でもある。従って、この不純物酸素は水素侵入サイトを塞いでしまうため、水素吸蔵量を減少させる原因となる。酸素と化合しやすいLnやYを添加すると、不純物酸素が主相の外に追いやられ、水素吸蔵量が増加するものと推定される。

【0033】本発明の水素吸蔵合金の各元素の原子比は、150℃以下の低温および大気圧近傍で高い水素吸蔵量を得るように検討して、上記のように決定された。次にその理由を説明する。なお、上記①式からわかるように、各元素の量はいずれも原子数比であり、合計が1である。

【0034】チタン(Ti)  
Ti量が増えると、合金主相である体心立方晶の格子寸法が拡大し、水素吸蔵量が増加する。高い水素吸蔵量を得るには、0.2以上のTiが必要であり、Ti量がこれより少ないと、水素吸蔵量が低くなる。チタンが多いほど水素

吸蔵量は増大するが、それに伴って水素平衡圧が低下し、室温・大気圧近傍で利用することができなくなる。

【0035】本発明では、水素平衡圧を上昇させる元素としてCrを添加するが、Ti量が0.5を越えると、Crを添加しても水素平衡圧を大気圧近傍まで上昇させることができなくなる。また、Ti量が多すぎると、微粉化が原因の繰り返し水素吸収・放出に対する寿命（耐久性）が低下する。水素吸蔵量と耐久性のバランスの観点から、Ti量は0.2以上、0.5以下とし、好ましくは0.3以上、0.45以下、より好ましくは0.3以上、0.4以下である。

#### 【0036】クロム (Cr)

Cr量が増えると水素吸蔵量は増加するが、その程度はTiほど大きくないので、Cr添加の主目的は水素平衡圧の制御にある。従って、Cr量は、Ti量や目的とする使用温度および水素平衡圧により変化する。しかし、Cr量が0.1未満では、Ti量が0.2の場合に室温での水素平衡圧が大気圧よりかなり低くなり、室温近傍で可逆的に水素を吸収・放出できなくなる。

【0037】一方、Crが0.4を超えると、第2相として析出するTiCr<sub>2</sub>相の量が増加し、水素吸蔵量が低下するだけでなく、微粉化が起こり易くなり繰り返し水素吸収・放出に対する寿命も低下する。水素吸蔵量と耐久性のバランスの観点から、Cr量は0.1以上、0.4以下とし、好ましくは0.2以上、0.4以下、より好ましくは0.2以上、0.35以下である。

#### 【0038】バナジウム (V)

Ti-Crの2元系では、第2相としてTiCr<sub>2</sub>が多く形成し、水素吸蔵量と繰り返し水素吸収・放出に対する寿命が低下し、水素平衡圧が低すぎて室温近傍での利用も困難になる。そのため、Vと一緒に添加する。Vの添加により、主相の体心立方晶相が多く得られ、水素吸蔵量が増加する。Vの量は、Ti、Cr、A元素、およびB元素の量により自動的に決定される。

#### 【0039】A元素 (Mn、Fe、Co、Cu、Nb、Zn、Zr、Mo、Ag、Hf、Ta、W、Al、Si、C、N、P、B)

これらの添加元素は、主相の体心立方晶を構成する金属である。Ti、Cr、Vのいずれかと置換し、格子寸法を拡大して水素吸蔵量を増加させるのに効果的な元素である。

【0040】個々の2元系状態図から予想されるように、これらの元素はTiまたはCrと金属間化合物、炭化物、ホウ化物を形成しやすいため、あまり多量には添加できない。A元素の量が0.2より多くなると、水素吸蔵量が少なくなか、水素を吸蔵しない、上記の金属間化合物等の化合物が多く形成されるため、かえって合金全体の水素吸蔵量が減少する。一方、A元素の量が0.01より少ないと、添加による水素吸蔵量の増加が認められない。

【0041】金属間化合物等の形成量と水素吸蔵量とのバランスから、A元素の量は0.01以上、0.2以下とし、好ましくは0.03以上、0.15以下、より好ましくは0.05以

上、0.15以下である。

#### 【0042】B元素 [Ln (ランタノイド系金属元素)、Y]

これらの添加元素は、合金の主相の水素侵入サイトに存在する不純物酸素と化合物を形成させるために添加する。従って、B元素の量は合金中の不純物酸素量に影響される。合金製造時に安価だが不純物の多い原料を用いれば多く添加する必要があり、高価だが不純物の少ない原料を用いれば少ない量で十分である。

10 【0043】工業的に安価に入手可能な原料を使用しても、合金の不純物酸素量は通常は1wt%以下であるが、スクラップ等の利用を考慮すると2wt%以上まで上昇することも考えられる。Ln、Yは、酸素と一般にB<sub>2</sub>O<sub>3</sub>型の酸化物を形成するため、不純物酸素と原子比で同等量程度添加すれば十分である。そのため、B元素の量の上限を0.03とした。これより多量にB元素を添加しても、水素吸蔵特性に大きな影響を与えない過剰のLn、Yを増やすだけでコスト増大につながる。

20 【0044】一方、B元素の量が0.001以下では、不純物酸素を除去できず、水素吸蔵量が増加しない。以上より、B元素の量を0.001以上、0.03以下とするが、上に説明したように、この量は合金の不純物酸素量、従って、使用する原料の純度により、この範囲内で増減させる。

【0045】このように、高価なB元素の添加量は非常に少ないので、その添加によるコスト増大はわずかである。また、B元素は主相の粒界で酸化物を形成するが、その量が上記のようにわずかであるので、それによる水素吸蔵量の悪影響は、この酸化物の添加による水素吸蔵量の増大に比べて少なくなる。また、これらの酸化物は、熱処理中の結晶粒度の粗大化を抑える効果を有しているため、B元素添加により、微細結晶組織を得ることができる熱処理温度の上限を、Ti-V-Cr合金の場合より高くすることができる。従って、熱処理時間が短くなる。

40 【0046】ランタノイド系金属は、純金属として精製されたLa、Ce等の元素を単独添加することも可能であるが、希土類金属の合金であり多くのランタノイド系金属を含んでいる安価なミッシュメタルと呼ばれる合金を用いると、本発明の水素吸蔵合金の製造コストはさらに低下する。

#### 【0047】主相の平均結晶粒径

以上に説明したように、本発明の水素吸蔵合金は、もともと水素吸蔵量の多い体心立方晶を主相とするTi-Cr-V系合金にA、Bの2種類の元素を添加して、さらに水素吸蔵量を増大させることに成功したものである。

【0048】しかし、このTi-Cr-V-A-B系の化学組成を持っても、この合金の水素吸蔵量は、製造方法や主相の平均結晶粒径により変化し、合金製造時に溶解した後の凝固速度（冷却速度）が遅くなって、主相の

平均結晶粒径が $40\mu\text{m}$ を超えると、同じ組成であっても水素吸蔵量が低下することが判明した。

【0049】これは、凝固速度が低下すると、 $\text{TiCr}_2$  や、前述したA元素との金属間化合物、炭化物、ホウ化物等の析出物の量が増大し、この析出物はそれ自体の水素吸蔵量が少ないか、水素を吸蔵しないため、その量が増えると合金全体としての水素吸蔵量は低下するためである。

【0050】また、 $\text{TiCr}_2$  や他の析出物の量が増えると、主相である体心立方晶の合金相中のTi、Cr量が低下するため、主相の水素吸蔵量が減少するだけでなく、主としてCr量減少に起因して、水素吸収・放出反応の平衡ガス圧である水素平衡圧が低下し、可逆的に吸収した水素を放出できなくなる。

【0051】さらに、合金製造時の凝固速度が遅くなると主相の平均結晶粒径が $40\mu\text{m}$ を超えると、繰り返し水素吸収・放出試験をした時の微粉化（粉末平均粒径の低下により判定できる）が顕著になり、合金寿命（耐久性）の低下も著しいことが判明した。この微粉化の主因は、上記の $\text{TiCr}_2$  やA元素との金属間化合物等の析出物を起点とする粒界破壊であると推定される。従って、凝固速度が遅くなって、このような析出物の量が増えると、微粉化の起点が多くなり、微粉化が起こり易くなるのである。

【0052】以上の知見から、本発明の水素吸蔵合金では、主相（体心立方晶）の平均結晶粒径を $40\mu\text{m}$ 以下に限定する。それにより、 $\text{TiCr}_2$  やA元素との金属間化合物等のような析出物の生成量が著しく低減するため、水素吸蔵量が多くなり、体心立方晶金属の理論上の最大水素吸蔵量に近づいた $H/M=1.80$ 以上の高い水素吸蔵量を示す合金が得られる。同時に繰り返し水素吸収・放出時の微粉化が起こりにくくなり、代表的な希土類系水素吸蔵合金である $\text{MmNi}_5$  系金属間化合物より著しく優れた繰り返し水素吸収・放出に対する耐久性を示すようになる。

【0053】本発明の水素吸蔵合金のこれらの特性をさらに改善するには、主相の平均結晶粒径が $20\mu\text{m}$ 以下、特に $15\mu\text{m}$ 以下であることが好ましい。また、第2相として形成される $\text{TiCr}_2$  やA元素との金属間化合物等の析出物の平均結晶粒径が $5\mu\text{m}$ 以下であると微粉化が生じにくくなり、 $2\mu\text{m}$ 以下であるとほとんど微粉化しないことが判明した。

【0054】主相の平均結晶粒径が $40\mu\text{m}$ 以下の本発明の水素吸蔵合金は、前述したように急冷凝固法により製造できる。具体的な急冷凝固の方法は、上記の平均結晶粒径を持つ合金が得られる限り限定されない。採用可能な急冷凝固法としては、回転電極法、回転ドラムあるいはロール上に合金溶湯を注湯する方法（例、単ロールまたは双ロール急冷法）、水冷銅板上へ薄く鋳込む方法、ガスアトマイズ法等が挙げられる。

【0055】これらのうち、回転電極法とアトマイズ法は、水素吸蔵合金の球形粉末を製造することができ、粉末化するための粉碎工程が不要となる上、粉末形状が実質的に球形で充填密度が高くなる点で有利である。他の方法の場合には、必要に応じて得られた水素吸蔵合金を粉碎して粉末にする。粉碎方法としては、水素化粉碎、機械粉碎のいずれも採用可能であり、両者を併用してもよい。

【0056】本発明の水素吸蔵合金は、平均粒径が $10\sim 50\mu\text{m}$ 程度の粉末形態とすることが適当である。それにより、表面積が増大し、水素の吸収・放出反応が促進される。必要であれば、分級により平均粒径を調整する。

【0057】急冷凝固法により製造された本発明の水素吸蔵合金は、微少な急冷歪みを持っている。この急冷歪みは本発明の水素吸蔵合金の耐久性（微粉化）に特に著しい悪影響は生じないが、所望により水素吸蔵合金を熱処理してこの急冷歪みを除去してもよい。この熱処理は、合金の酸化を防止するため、真空中または不活性ガス中で行うことが好ましい。

【0058】熱処理条件は、熱処理中に合金主相の平均結晶粒径が $40\mu\text{m}$ より大きくなることないように設定する必要がある。この条件は、急冷凝固法により製造された水素吸蔵合金の主相の平均結晶粒径によっても異なるが、通常は温度 $400\sim 1000^\circ\text{C}\times 1\sim 20$ 時間の範囲内であろう。但し、熱処理温度が例えば $900^\circ\text{C}$ 以上と高い場合には、熱処理時間を短くして、熱処理後の合金主相の平均結晶粒径が $40\mu\text{m}$ を超えないようにする。 $\text{Ti-V-Cr}$ 合金の熱処理温度は一般に $750^\circ\text{C}$ 以下であるので、B元素の添加により熱処理温度の上限を高くできる。

【0059】後述するように、本発明の水素吸蔵合金の耐酸化性を向上させるため、合金表面に $\text{Ti-Ni}$ 化合物を主体とするNi付加層を形成する場合には、この層の形成過程で熱処理を行うことがあり、この熱処理中に急冷歪みも除去される。従って、その場合には、急冷歪みの除去の目的だけの熱処理は必要ない。

【0060】本発明の水素吸蔵合金は、大気中に放置しておくと、室温近傍の低温（例、 $80^\circ\text{C}$ ）で測定した水素吸収量が減少することがある。即ち、この合金を大気中に放置すると表面が酸化し、この酸化膜が障害となって低温での水素吸蔵量が減少するものと考えられる。このように大気放置により水素吸蔵量が低下した水素吸蔵合金は、高圧水素ガス中（例、 $20$ 気圧）で $500^\circ\text{C}$ まで加熱して活性化させると水素吸収量が増加し、放置前の吸収量を回復する。しかし、前述したように、この活性化処理は費用がかかる。

【0061】水素吸蔵合金を利用した装置では、製作過程で大気との接触を完全に避けることはできないので、上記の活性化処理を避けるには、大気と接触しても酸化しないように本発明の水素吸蔵合金の耐酸化性を改善することが望ましい。

【0062】この点について検討した結果、特開昭60-190570号公報に記載のように、本発明の水素吸蔵合金の表面をNiで被覆すると、合金の耐酸化性が改善されることが判明した。しかし、この手法は耐酸化性の向上には有効であるものの、合金表面を被覆したNi自体は水素吸蔵能力がほとんどないため、合金単位重量当たりの水素吸収量が低下する。

【0063】そこでさらに検討した結果、合金表面のNi被覆層を母材となるTi-V-Cr-A-B系合金と反応させてTi-Ni化合物を主体とするNi付加層に変え、このNi付加層は純Niより大きな水素吸蔵能力を持つため、水素吸収量をほとんど低下させずに、水素吸蔵合金に耐酸化性を付与することができることがわかった。従って、好適態様においては、本発明の水素吸蔵合金はTi-Ni化合物を主体とするNi付加層を合金表面に有している。それにより、水素吸蔵量を実質的に低下させずに耐酸化性が向上し、上述した活性化処理が不要となるか、あるいは非常に軽減される。

【0064】合金表面へのNiの被覆方法は、物理的な方法（例、Ni微粉末と合金粉末とを混合する方法、ボールミル等で混合させるメカニカルアロイングに相当する方法も含む）、化学的な方法（例、電解Niめっき、無電解Niめっき）のいずれでもよく、特に制限はない。Niの被覆量は、水素吸蔵合金の粉末平均粒径によっても異なるが、通常は水素吸蔵合金に対して1~20重量%、好ましくは5~10重量%が適当である。このNi被覆の前に、必要であれば、水素吸蔵合金をフッ酸、塩化水素酸などの非酸化性の酸で酸洗処理して、合金表面の酸化層を除去してもよい。

【0065】水素吸蔵合金の表面をNiで被覆した後、熱処理して表面被覆中のNiを母材合金中のTi成分とを反応させて、Ni層を水素吸蔵能力の高いTi-Ni化合物に変化させることにより、表面にTi-Ni化合物を主体とするNi付加層を形成する。このNi付加層は母材からCrを取り込んでいるため、Ti-Niの2元系金属間化合物より耐酸化性に優れている。

【0066】この熱処理も、合金の酸化を防止するため、真空中または不活性ガス中で行うことが好ましい。熱処理条件は、この熱処理中に母材合金の主相の平均結晶粒径が40 $\mu$ mを超えるまでに粗大化しないように設定する。この観点から、熱処理温度は400~1000 $^{\circ}$ Cの範囲とし、熱処理時間は上記の粗大化が起こらないように設定する。熱処理温度が1000 $^{\circ}$ Cを越えると、平均結晶粒径が第2相の析出物の粗大化が進み、水素吸収量が低下したり、水素吸収・放出に繰り返すにより微粉化し易くなる。一方、400 $^{\circ}$ C未満ではTi-Ni化合物の生成反応が進みにくい。好ましい熱処理温度は450~900 $^{\circ}$ Cである。

【0067】但し、Ni被覆を、例えばボールミル中で長時間（例、100~1000時間）行うといったメカニカルアロイング法により行った場合には、生成したNi被覆は既

に母材合金中のTiと反応してTi-Ni化合物を主体とするNi付加層になっているので、反応のために熱処理を行う必要はない。

【0068】

【実施例】試験合金の作製には、高周波溶解法（5 kg/ch）、ボタンアーク溶解法（ボタンサイズ：250 g/chと50 g/ch）、銅ロールを用いた単ロール急冷法（20 g/ch）、Arガスアトマイズ法（10 g/ch）、または回転電極法（50 g/ch）を用いた。合金溶湯の調製に用いた原料は、純度99wt%のスポンジチタン、純度98wt%のバナジウム、純度99wt%のクロム、ランタノイド系希土類金属の合金であるミッシュメタル（Lnと略記する）（La=46wt%、Ce=5wt%、Nd=37wt%、Pr=10wt%、総希土類含有量99.5wt%）、純度99wt%のFe、Mn、Co、Nb、Y、Zn、Zr、純度99.9wt%のAl、Ag、Hf、Ta、W、Mo、Cuであった。軽元素（Si、C、N、P、B）は、TiまたはCrとの化合物（TiC、TiB<sub>2</sub>等）で添加した。

【0069】粉末が直接得られるガスアトマイズ法と回転電極法以外の方法では、得られた合金を300 $^{\circ}$ C、2.5 MPaの水素ガス中で5時間水素化した後に機械的に粉砕し、粉末にした。いずれの合金粉末も、100 $\mu$ m以下の粉末をふるいで選別して用いた。ガスアトマイズ材の一部については、平均結晶粒径を大きくするために、アルゴン雰囲気中で熱処理を施した。試験合金の特性評価方法を次にまとめて説明する。

【0070】水素ガス吸収・放出特性

水素ガス吸収・放出特性は、ジベルツ型装置を用いて活性化原点法により測定した。測定は、試験合金を容器に入れ、真空排気して原点を決定した後、3.0 MPaの水素圧下300~500 $^{\circ}$ Cに加熱して活性化処理してから行った。機械的粉砕における合金粉末表面の酸化の影響を除くため、活性化処理の前に試験合金を5 vol%弗化水素酸（フッ酸）水溶液で酸洗した。

【0071】測定に用いた水素放出・吸収サイクルは、温度80 $^{\circ}$ Cで、水素圧を3.0 MPaから0.01 MPaまで下げる水素ガス放出と、水素圧を0.01 MPaから3.0 MPaまで加圧する水素ガス吸収とからなる。

【0072】水素吸蔵量は、1サイクル目の水素ガス放出時に水素放出曲線を作製して、圧力1 MPaでの水素吸蔵量の値を求め、この水素量を合金を構成する金属原子数に対する吸収された水素原子数の比であるH/Mに換算することにより評価した。H/Mが1.80以上を合格とした。

【0073】繰り返し水素吸収・放出による微粉化  
繰り返し水素吸収・放出による微粉化の影響は、前記の水素放出・吸収サイクルを300サイクル行った後、粒径20 $\mu$ m以下の粉末がどれだけ増加したかを測定し、評価した。粒度測定には、レーザー回折式の粒度分布測定装置を用いた。製造方法により粉末の粒度分布に差があったため、評価は試験前の20 $\mu$ m以下の粒子量を基準にし



て、その量に対して比較した微粉増加率を次式により算出して評価した。微粉増加率が15%以下であれば合格である。

【0074】

【数1】

$$\text{微粉増加率(\%)} = \left[ \frac{A-B}{B} \right] \times 100$$

A=300 サイクル試験後の20 $\mu$ m以下の粉末量。  
B=試験前の20 $\mu$ m以下の粉末量。

#### 【0075】結晶粒径

試験合金の主相の結晶粒径の測定は、粉碎前の合金をエポキシ樹脂に埋め込み、研磨した後に、0.4 vol%フッ酸と1 vol%硝酸との混酸でエッチングし、光学顕微鏡で観察を行い、ランダムに選択した結晶粒20個の測定結果の平均値を平均結晶粒径とした。第2相の析出物の粒径は微細であったため、SEM（二次電子顕微鏡）を用いて測定し、上と同様に平均値を求めた。

#### 【0076】耐酸化性

表面をNi被覆してNi付加層を形成した水素吸蔵合金の耐酸化性の評価は、温度25℃、湿度65%の恒温恒湿の空気雰囲気、1週間放置した後、ジーベルツ型の水素吸収・

放出試験装置を用いて、活性化処理なしに80℃で3.0 MPaの水素ガスの吸収試験を行い、Ni付加層を形成する前の合金の水素吸蔵量と比較した水素吸蔵量の低下率を、次式により算出した。水素吸蔵量の低下率が10%以下であれば合格である。

【0077】

【数2】

$$\text{水素吸蔵量低下率(\%)} = \left[ \frac{C-D}{C} \right] \times 100$$

10

C=Ni被覆前に活性化処理して測定した水素吸蔵量  
D=1週間放置後に70℃で測定した水素吸蔵量

【0078】（実施例1）本実施例は、合金組成を変化させて水素吸蔵合金の性能を検討した実施例である。水素吸蔵合金の作製法としては、急冷凝固法のみを採用したので、主相の平均結晶粒径はいずれも40 $\mu$ m以下であり、多くは20 $\mu$ m以下であった。各合金の水素吸蔵量と微粉増加率の測定結果を、合金組成および作製法とともに表1に示す。

20 【0079】

【表1-1】

試験 No	化 学 組 成					溶解方法	水素 吸蔵量 (H/M)	微粉 増加率 (%)	備 考
	Ti	V	Cr	A	B				
1	0.30	0.37	0.30	Mn:0.02	Ln:0.01	酸7)74X	1.81	8	本 発 明 例
2	0.30	0.29	0.30	Mn:0.10	Ln:0.01	"	1.84	9	
3	0.30	0.21	0.30	Mn:0.18	Ln:0.01	"	1.82	10	
4	0.30	0.37	0.30	Fe:0.02	Ln:0.01	"	1.81	9	
5	0.30	0.21	0.30	Fe:0.18	Ln:0.01	"	1.81	13	
6	0.30	0.37	0.30	Co:0.02	Ln:0.01	"	1.81	8	
7	0.30	0.21	0.30	Co:0.18	Ln:0.01	"	1.82	11	
8	0.30	0.37	0.30	Cu:0.02	Ln:0.01	"	1.81	10	
9	0.30	0.21	0.30	Cu:0.18	Ln:0.01	"	1.82	12	
10	0.30	0.37	0.30	Nb:0.02	Ln:0.01	"	1.82	8	
11	0.30	0.21	0.30	Nb:0.18	Ln:0.01	"	1.84	14	
12	0.30	0.37	0.30	Zr:0.02	Ln:0.01	"	1.81	8	
13	0.30	0.21	0.30	Zr:0.18	Ln:0.01	"	1.83	13	
14	0.30	0.37	0.30	Mo:0.02	Ln:0.01	"	1.81	9	
15	0.30	0.21	0.30	Mo:0.18	Ln:0.01	"	1.81	12	
16	0.30	0.37	0.30	Ta:0.02	Ln:0.01	"	1.82	8	
17	0.30	0.21	0.30	Ta:0.18	Ln:0.01	"	1.83	13	
18	0.30	0.37	0.30	Al:0.02	Ln:0.01	"	1.81	10	
19	0.30	0.21	0.30	Al:0.18	Ln:0.01	"	1.81	14	
20	0.30	0.37	0.30	Si:0.02	Ln:0.01	"	1.81	8	
22	0.30	0.21	0.30	Si:0.18	Ln:0.01	"	1.83	11	
23	0.30	0.29	0.30	Ag:0.10	Ln:0.01	"	1.82	8	
24	0.30	0.29	0.30	Hf:0.10	Ln:0.01	"	1.83	9	
25	0.30	0.29	0.30	W :0.10	Ln:0.01	"	1.81	12	
26	0.30	0.25	0.30	Mn:0.07 Fe:0.07	Ln:0.01	"	1.84	10	
27	0.30	0.25	0.30	Fe:0.07 Cu:0.07	Ln:0.01	"	1.84	11	
28	0.30	0.25	0.30	Co:0.07 Nb:0.07	Ln:0.01	"	1.85	11	
29	0.30	0.27	0.30	Mn:0.05 Hf:0.05 C :0.02	Ln:0.01	"	1.82	8	
30	0.30	0.27	0.30	Nb:0.05 W :0.05 N :0.02	Ln:0.01	"	1.83	9	
31	0.30	0.27	0.30	Zr:0.04 Si:0.04 P :0.04	Ln:0.01	"	1.82	11	
32	0.30	0.27	0.30	Zr:0.04 Mn:0.04 B :0.04	Ln:0.01	酸7)74X	1.84	10	

[0080]

[表 1-2]

試験 No.	化学組成					溶解方法	水素 吸蔵量 (H/M)	微粉 増加率 (%)	備考
	Ti	V	Cr	A	B				
33	0.30	0.24	0.30	Mn:0.05 Fe:0.05 Cu:0.05	Ln:0.01	"	1.86	10	本 発 明
34	0.30	0.24	0.30	Fe:0.05 Co:0.05 Nb:0.05	Ln:0.01	"	1.86	10	
35	0.30	0.256	0.30	Fe:0.14	Ln:0.004	"	1.81	9	
36	0.30	0.235	0.30	Fe:0.14	Ln:0.025	"	1.82	9	
37	0.30	0.25	0.30	Fe:0.14	Ln:0.01	"	1.83	8	
38	0.30	0.25	0.30	Fe:0.14	Ln:0.01	0-1 急冷	1.83	8	
39	0.30	0.25	0.30	Fe:0.14	Ln:0.01	回転電極	1.83	10	
40	0.30	0.24	0.30	Fe:0.05 Co:0.05 Nb:0.05	Ln:0.01	0-1 急冷	1.85	10	
41	0.30	0.24	0.30	Fe:0.05 Co:0.05 Nb:0.05	Ln:0.01	回転電極	1.85	12	
42	0.25	0.40	0.20	Fe:0.14	Ln:0.01	0-1 急冷	1.81	8	例
43	0.48	0.10	0.38	Fe:0.03	Ln:0.01	"	1.84	13	
44	0.48	0.10	0.38	Fe:0.03	Y:0.01	"	1.85	11	
45	0.48	0.10	0.38	Fe:0.03	Ln:0.005 Y:0.005	"	1.85	10	
46	0.30	0.40	0.30	—	—	"	1.71	8	
47	0.30	0.15	0.30	Mn:0.24	Ln:0.01	"	1.65	18	比 較
48	0.30	0.15	0.30	Fe:0.24	Ln:0.01	"	1.52	20	
49	0.30	0.15	0.30	Co:0.24	Ln:0.01	"	1.55	17	
50	0.30	0.15	0.30	Cu:0.24	Ln:0.01	"	1.51	22	
51	0.30	0.15	0.30	Nb:0.24	Ln:0.01	"	1.45	18	
52	0.30	0.15	0.30	Mn:0.10 Fe:0.10 Cu:0.04	Ln:0.01	"	1.50	23	
53	0.30	0.15	0.30	Fe:0.10 Co:0.10 Nb:0.04	Ln:0.01	"	1.48	21	
54	0.30	0.225	0.30	Mn:0.14	Ln:0.035	"	1.66	8	例
55	0.16	0.57	0.12	Fe:0.14	Ln:0.01	"	0.85	12	
56	0.30	0.47	0.08	Fe:0.14	Ln:0.01	"	1.41	13	
57	0.60	0.13	0.12	Fe:0.14	Ln:0.01	"	1.52	20	
58	0.30	0.10	0.45	Fe:0.14	Ln:0.01	"	0.78	19	
59	0.30	0.16	0.30	Mn:0.24	—	"	1.76	18	
60	0.30	0.39	0.30	—	Ln:0.01	"	1.75	9	

【0081】表1からわかるように、合金組成が本発明の範囲内である水素吸蔵合金はいずれも、80℃という室温近傍の比較的低い温度で、H/Mが1.80以上という高い水素吸蔵量を示し、また繰り返し水素吸収・放出試験による微粉化率が15%以下と低く、室温近傍でも水素吸蔵量が多く、かつ繰り返し水素吸収・放出による劣化が少ないことがわかる。

【0082】これに対して、A、B両元素を添加しなかったNo.46の合金では水素吸蔵量が低かった。A、Bの一方の元素だけを添加したNo.59, 60でも、水素吸蔵量の増大は不十分であった。A元素の添加量が多すぎたNo.47~53の合金では、水素吸蔵量の低下と同時に、微粉化率も増大した。B元素の添加量が多すぎたNo.54の合金では、水素吸蔵量が低下した。A、B両元素の添加量が適切でも、Ti、Cr、Vの含有量が本発明の範囲外で

あるNo.55~58の合金は、いずれも水素吸蔵量が低く、またTiやCrの量が多すぎると、微粉化率が大きくなった。

【0083】(実施例2)本実施例は、各種製造方法で作製した主相の平均結晶粒径が異なる水素吸蔵合金について、主相の平均結晶粒径が水素吸蔵合金の性能に及ぼす影響を検討した実施例である。水素吸蔵合金の化学組成は、Ti=0.30、V=0.24、Cr=0.30、A=0.15 (Mn=0.04、Fe=0.03、Cu=0.03、Al=0.03、B=0.05)、B=0.01 (Ln=0.01)の同一組成とした。結晶粒径の影響をみるため、ガスアトマイズ後に熱処理した試験合金も作製した。試験結果を表2に示す

【0084】

【表2】

試験 No.	溶 解 方 法	立方晶主相 の結晶粒径 ( $\mu\text{m}$ )	析出物の 結晶粒径 ( $\mu\text{m}$ )	水素 吸蔵量 (H/W)	微粉 増加率 (%)	備 考
1	ガスアトマイズ	16	0.6	1.86	10	本 発 明 例
2	ロール急冷	15	0.5	1.86	9	
3	回転電極	15	0.6	1.85	10	
4	ガスアトマイズ 熱処理: 680℃ $\times$ 10hr	30	1.7	1.82	13	
5	ガスアトマイズ 熱処理: 950℃ $\times$ 2hr	35	2.1	1.84	15	
6	ボタンアーク溶解, 50g	48	4.5	1.60	21	比 較 例
7	ボタンアーク溶解, 250g	70	9.5	1.55	25	
8	高周波溶解, 5kg	85	10.6	1.25	32	
9	ガスアトマイズ 熱処理: 900℃ $\times$ 15hr	45	4.2	1.55	20	
10	ガスアトマイズ 熱処理: 1300℃ $\times$ 10hr	65	5.5	1.40	33	

【0085】表2からわかるように、急冷凝固法で水素吸蔵合金を作製すると、主相の平均結晶粒径が20 $\mu\text{m}$ 以下の微細な組織の合金が得られる。この微細組織の水素吸蔵合金を熱処理すると、結晶粒径は粗大になるが、主相の平均結晶粒径が40 $\mu\text{m}$ 以下であれば、水素吸蔵量と微粉増加率のいずれも合格であった。本発明の合金では、950℃という高温の熱処理でも、短時間で平均結晶粒径を40 $\mu\text{m}$ 以下であれば、熱処理による水素吸蔵量や微粉増加率への悪影響はない。ただし、急冷凝固後に熱処理していない、平均結晶粒径が20 $\mu\text{m}$ 以下の合金の方が成績がよく、水素吸蔵量も高い上、微粉増加率が10%以下となった。

【0086】また、表2から、主相の平均結晶粒径が40 $\mu\text{m}$ 以下であると、第2相の析出物の平均結晶粒径も5 $\mu\text{m}$ 以下、特に2 $\mu\text{m}$ 以下という、微粉化の抑制の望ましい範囲になることもわかる。

【0087】一方、凝固速度の遅いボタンアーク溶解材や高周波溶解材は、主相の平均結晶粒径が40 $\mu\text{m}$ を超え、水素吸蔵量と微粉増加率のいずれも不合格となった(No. 6~8)。ガスアトマイズ材を熱処理した場合も、平均結晶粒径が40 $\mu\text{m}$ を超えるように熱処理条件を設定すると、やはり水素吸蔵量と微粉増加率のどちらも大きく低下した(No. 9, 10)。

【0088】(実施例3)本実施例は、合金表面にTi-Ni化合物を主体とするNi付加層を形成した場合の水素吸蔵合金の耐酸化性の向上を例示する。試験した水素吸蔵合金はいずれも、Arガスアトマイズ法で作製した粉末である。合金の化学組成は、Ti=0.30、V=0.25、Cr=0.30、A=0.14、B=0.01の同一組成とした(但し、A、Bの元素種類は変動)。

【0089】Ni付加層を形成するための水素吸蔵合金粉末のNi被覆は、物理的な方法と化学的な方法の両方を採用した。物理的な方法では、粒径1 $\mu\text{m}$ 程度のNi微粉末を用い、これを合金粉末に対して10重量%配合した後、乳鉢で均一に混合するか、またはボールミルで長時間混合した。化学的な方法は、市販の無電解Niめっき液を用いて、合金粉末表面に約10重量%のNiめっき層を形成した。なお、当然ながら、電解めっきを行っても同様のNiめっき層を形成することができる。

【0090】これらの方法でNi被覆を施した後、アルゴン雰囲気中で熱処理を行って、Ni被覆層を合金粉末と反応させて合金化することにより、合金表面にTi-Ni化合物を主体とするNi付加層を形成した。但し、ボールミルによりNi粉末を機械的に被覆する方法では、このボールミル混合を100時間と長時間行うことにより、メカニカルアロイングによってNi被覆の合金化が起こっているの  
30 で、熱処理は行わなかった。また、比較例として、この熱処理を行わず、単にNi被覆(無電解Niメッキまたは乳鉢混合)しただけの試験材も作製した。

【0091】こうして表面にNi含有層を形成したガスアトマイズ法で作製された水素吸蔵合金粉末の耐酸化性を、上記のように所定条件の大気中で1週間の放置後に活性化処理せずに水素吸蔵量を測定することにより調査した。試験結果を、Ni付加層の形成方法(上段はNi被覆方法、下段は熱処理条件)、主相の平均結晶粒径、Ti-Ni化合物相の形成の有無(X線回折で確認)と共に表3  
40 に示す。

【0092】

【表3】

試験 No.	化学組成 <sup>1)</sup>		作製方法	Ni含有相形成 上: Ni付着法 下: 熱処理	平均 結晶 粒径	Ti-Ni 化合物 相形成	吸蔵量 低下率 (%)	備 考
	A	B						
1	Mn:0.07 Fe:0.07	Ln:0.01	#777777	無電解めっき 680℃×10hr	27 $\mu$ m	有	7	本 発 明 例
2	Mn:0.07 Fe:0.07	Ln:0.01	"	Ni粉末混合 680℃×10hr	27 $\mu$ m	有	10	
3	Mn:0.07 Fe:0.07	Ln:0.01	"	Ni粉末混合 6-4 $\mu$ m 100hr	15 $\mu$ m	有	9	
4	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき 400℃×10hr	20 $\mu$ m	有	6	
5	Co:0.07 Nb:0.07	Y:0.01	"	無電解めっき 680℃×25hr	23 $\mu$ m	有	5	
6	Zr:0.07 Ta:0.07	Y:0.01	"	無電解めっき 680℃×25hr	32 $\mu$ m	有	9	
7	Fe:0.04 Ta:0.04 Al:0.03 Si:0.03	Ln:0.01	"	無電解めっき 680℃×10hr	25 $\mu$ m	有	7	
8	Mn:0.04 Al:0.04 C:0.03 B:0.03	Ln:0.01	"	無電解めっき 680℃×10hr	23 $\mu$ m	有	8	
9	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき 950℃×2hr	33 $\mu$ m	有	7	比 較 例
10	Mn:0.07 Fe:0.07	Ln:0.01	#777777	なし	15 $\mu$ m	—	35	
11	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき	15 $\mu$ m	無	19	
12	Mn:0.07 Fe:0.07	Ln:0.01	"	Ni微粉末混合	15 $\mu$ m	無	24	
13	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき 900℃×10hr	42 $\mu$ m	有	22	

<sup>1)</sup> Ti=0.30、V=0.25、Cr=0.30、A=0.14、B=0.01

【0093】表3からわかるように、本発明に従ってNi被覆を施し、かつこのNi被覆を合金成分と反応させることによりTi-Ni化合物を主体とするNi付加層を合金表面に形成すると、本発明の水素吸蔵合金の大気中での酸化が抑制され、1週間放置後に活性化処理せずに水素吸蔵量を測定しても、水素吸蔵量の低下が10%以下に抑えられた。即ち、大気中で水素吸蔵合金の粉末を取り扱っても表面がほとんど酸化されないの、取扱いが非常に容易になり、また費用のかかる活性化処理が不要ないし軽減される。

【0094】一方、比較例において、Ni被覆を全く施さない、1週間放置後の合金粉末の水素吸蔵量は35%も低下した(No.9)。しかし、Ni被覆を施しても、熱処理またはメカニカルアロイングによりNi被覆を合金成分と反応させないと、1週間放置後の合金粉末の水素吸蔵量は19~24%も低下した(No.10, 11)。即ち、Ni被覆だけでは、未被覆の場合に比べて耐酸化性の向上は著しく少ないことがわかる。また、Ni被覆後の反応のための熱処理条件が不適切で、主相の平均結晶粒径が40 $\mu$ mを超える

と、粗大化の影響で水素吸蔵量はやはり大きく低下した。

【0095】

【発明の効果】本発明の水素吸蔵合金は、水素吸蔵量がH/M=1.80以上と非常に高く、室温近傍の比較的低い温度(例、150℃以下)で水素の吸収・放出が起こるので、各種用途に使い易く、水素吸収・放出を長期間にわたって繰り返しても微粉化しにくいので、高い水素吸蔵量が長期間保持され(耐久性に優れ)、かつ比較的安価である。

【0096】また、合金表面にTi-Ni化合物を主体とするNi付加層を形成すると、合金の耐酸化性が著しく向上し、大気中に放置した時の水素吸蔵量の低下が非常に小さくなるので、大気中で容易に取り扱うことが可能となり、費用のかかる活性化処理が不要となるか、軽減される。従って、本発明の水素吸蔵合金は、水素ガス貯蔵・輸送用、水素ガス分離・精製用、熱輸送システムや冷却システム、静的コンプレッサーといった用途に最適である。

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**CLAIMS**

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[Claim(s)]

[Claim 1] Formula:  $Ti_a V_{1-a-b-c-d} Cr_b Al_c B_d \dots$  Hydrogen storing metal alloy which has the composition shown by \*\*, and is characterized by the diameter of average crystal grain of the main phase being 40 micrometers or less. A among the above-mentioned formula Mn, Fe, Co, Cu, Nb, Zr, Mo, One sort or two sorts or more of elements chosen from Ag, Hf, Ta, W, aluminum, Si, C, N, P, and B are meant. B is Ln (lanthanoids system metal). Meaning one sort or two sorts or more of elements which reached and were chosen from Y, the value of a is 0.2. It is 0.5 above. The value of the following and b is 0.1. It is 0.4 above. The value of the following and c is 0.01 or more and 0.2. The value of the following and d is 0.001. It is 0.03 or less above.

[Claim 2] The hydrogen storing metal alloy according to claim 1 which has nickel addition layer which makes a Ti-nickel compound a subject on a front face.

[Claim 3] \*\* The manufacture method of a hydrogen storing metal alloy according to claim 1 characterized by manufacturing an alloy with the composition shown by the formula by the rapid solidification method.

[Claim 4] \*\* an alloy with the composition shown by the formula -- a rapid solidification method -- manufacturing -- the front face of this hydrogen storing metal alloy -- nickel -- covering -- subsequently -- The manufacture method of a hydrogen storing metal alloy according to claim 2 characterized by heat-treating at the temperature of 400-1000 degrees C.

[Claim 5] \*\* The manufacture method of a hydrogen storing metal alloy according to claim 2 which manufactures an alloy with the composition shown by the formula by the rapid solidification method, and consists of the mechanical alloying method covering the front face of this hydrogen storing metal alloy with nickel.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

[0001]

[The technical field to which invention belongs] this invention is the amount of hydrogen absorption. (hydrogen-absorption capacity) Highly and simultaneous, repeatedly, it is few, and property degradation by hydrogen absorption discharge can use at the temperature near the room temperature, and is related with the hydrogen storing metal alloy with the feature of being comparatively cheap excellent in endurance, and its manufacture method. The hydrogen storing metal alloy of this invention with these features is an object for hydrogen gas storage / transportation, and an object for hydrogen gas separation / refining, and especially the further is the the best for a heat-transport system, a cooling system, a static compressor, etc.

[0002]

[Description of the Prior Art] If hydrogen gas burns, in order that it may become water and may form neither carbon dioxide gas nor a sulfur oxide like a fossil fuel, it is a clean energy source.

[0003] Generally storage and transportation of hydrogen gas are compressed, and is performed as a high pressure gas. The cold-storage container of -253 \*\* is required for storage of liquid hydrogen, and the top where an evaporation loss is also large, since a lot of energy is required for liquefaction of hydrogen, it liquefies like nitrogen and stores because it is difficult. However, it is volume although the proof-pressure container which is heavy and is bulky is required for high-pressure hydrogen gas. It does not become about 1/200, but when it is inefficient-like, there is a problem also in safety.

[0004] Then, using for storage and transportation of hydrogen gas the hydrogen storing metal alloy which can absorb and emit hydrogen gas in reversible by cooling and heating has been examined. The storage density of a hydrogen storing metal alloy of the hydrogen gas per unit volume is higher than a high-pressure hydrogen gas container, it becomes more nearly lightweight and the hydrogen gas storage container of a snug product, and transportation of hydrogen gas also becomes easy. Moreover, since it is low voltage, safety is high and strong also against the mechanical shock under transportation.

[0005] The hydrogen storing metal alloy aiming at storage and transportation of hydrogen is developed conventionally, and is already used for storage of small-scale hydrogen. Moreover, the research of a low-pollution hydrogen fueled car which uses hydrogen gas as an alternate fuel of a gasoline is also progressing, and various kinds of hydrogen storing metal alloys including a FeTi system are examined by this as a hydrogen storage device.

[0006] There is other the following in the use it is expected that utilization of a hydrogen storing metal alloy is. Absorption of the hydrogen of a hydrogen storing metal alloy (hydrogenation) Discharge (decomposition of a hydride) It is a reversible reaction accompanied by discharge and absorption of heat, and has a heat-chemical energy conversion function. It can be used for a cooling system using this function as storage and the space transportation system, and the chemical heat pump of heat energy.

[0007] Moreover, if the hydrogen storing metal alloy which made hydrogen gas absorb at low temperature is heated to an elevated temperature, high-pressure hydrogen gas will be emitted. The function in which this transforms heat energy into mechanical energy is also achieved. This function can be used as heat drive type a static hydrogen compressor and an actuator.

[0008] Absorption / discharge speed of the hydrogen gas of a hydrogen storing metal alloy is larger than absorption / discharge speed of other gas constituents, and has a difference also between hydrogen isotopes. Therefore, hydrogen separation of isotopes is possible for separation of the high grade hydrogen gas from mixed gas, refining of impure hydrogen gas, and a further by using a hydrogen storing metal alloy and making hydrogen or a specific hydrogen isotope absorb or emit alternatively.

[0009] Thus, although there is a broad use in a hydrogen storing metal alloy, hydrogen storage capacity is the most



important property to every use. Moreover, since the above-mentioned use needs comparatively a lot of hydrogen storing metal alloys for all, even if it repeats and uses a hydrogen storing metal alloy, there are few depressions and it is important to excel in endurance and that the price of an alloy is also comparatively cheap. Depending on a use, it is the comparatively low temperature near the room temperature. (an example and below 150 \*\*) It is also called for that absorption and discharge of hydrogen take place.

[0010] For example, LaNi<sub>5</sub> which utilization preceded Or MmNi<sub>5</sub> AB<sub>5</sub> represented Since the hydrogen storing metal alloy of type is expensive, even if the amount of the hydrogen storing metal alloy used can use it for small rechargeable batteries, such as a few Ni-H battery, a price side to use is difficult for it for the use which needs a lot of hydrogen storing metal alloys called the object for hydrogen gas storage. Moreover, there is not so much hydrogen storage capacity.

[0011] To JP,59-38293,B, it is comparatively cheap, and the Ti-Cr-V system alloy is indicated as a hydrogen storing metal alloy with much hydrogen storage capacity. As the manufacture method of an alloy, only the arc process is explained concretely. The hydrogen storing metal alloy which consists of the same components also as JP,7-252560,A is indicated. The analogous hydrogen storing metal alloy of a Ti-V-nickel system is indicated by JP,7-268513,A and JP,7-268514,A.

[0012] Moreover, by covering copper and/or a nickel metal with wet electroless deposition to hydrogen storing metal alloy powder, influence of contamination by the impurity gas in atmosphere can be made small, and the thing with unnecessary initial-activity-izing which it is and can be mitigated by carrying out is explained to JP,60-190570,A.

[0013] [Problem(s) to be Solved by the Invention] Absorption and discharge of the hydrogen gas of a hydrogen storing metal alloy are a chemical reaction accompanied by expansion and contraction of volume, respectively. In order to obtain a practical reaction rate, it needs to be powdered and it is necessary to use a hydrogen storing metal alloy and to increase a surface area. However, if expansion and contraction of the volume in the end of an alloy powder are repeated during use, a crack will go into powder by internal distortion, it will be soon divided into a fine particle, and powder will carry out pulverization. If pulverization advances, hydrogen gas will not flow easily by lock out, or fines will be mixed with the flow of hydrogen gas and will move into gas piping. Therefore, this pulverization is long-term repeat hydrogen absorption / discharge life of a hydrogen storing metal alloy. (namely, endurance) It becomes the big cause of a fall.

[0014] Although the Ti-Cr-V system hydrogen storing metal alloy and Ti-V-nickel system alloy which were mentioned above are developed as an alloy with much hydrogen storage capacity, predetermined hydrogen storage capacity is not reached in many cases in fact, and the problem of the endurance by the above-mentioned pulverization cannot be solved, either.

[0015] For example, when it manufactures by the arc process as indicated by this official report, since solidification speed is slow, a Ti-Cr-V system hydrogen storing metal alloy given in JP,59-38293,B is low TiCr<sub>2</sub> of hydrogen storage capacity as the 2nd phase. An intermetallic compound deposits at a remarkable rate and hydrogen storage capacity falls. Moreover, a crack enters with this 2nd phase as the starting point into the repeat of hydrogen absorption and discharge in the end of an alloy powder, and there is also a trouble that pulverization is promoted.

[0016] After it holds a hydrogen storing metal alloy given in JP,7-252560,A at the elevated temperature of 1200-1400 degrees C in order to reduce the 2nd above-mentioned phase, and it considers as a cubic single phase organization in the example, the process which quenches with water cooling immediately is taken. However, since big and rough-ization of crystal grain arises in the case of heating-at-high-temperature maintenance, even if the amount of deposits of the 2nd phase decreases, the intensity of the material itself becomes weak by big and rough-ization, and it becomes easy to carry out pulverization of it by this method. In case it moreover mass-produces industrially, in order to use a large-sized ingot, also with water cooling, sufficient cooling rate is not obtained, but the big and rough sludge of the 2nd phase which makes a Ti-Cr compound a subject is formed, and hydrogen storage capacity also falls.

[0017] A Ti-V-nickel system hydrogen storing metal alloy given in each official report of JP,7-268513,A and 7-268514 is the Ti Ni alloy phase of the 2nd phase, or AB<sub>2</sub> to the grain boundary of the host phase which consists of a Ti-V system alloy. A type RABESU alloy phase has the organization in which the 3-dimensional mesh frame was formed. In order that this grain-boundary phase may raise reactivity with the hydrogen of an alloy, even if a host phase has some oxidization, absorption and discharge of hydrogen gas are possible through this grain-boundary phase. However, in order to deposit the 2nd low phase of hydrogen-absorption capacity in a large quantity so that the 3-dimensional network structure is formed, the hydrogen quantity to be stored of the whole alloy falls. Moreover, the problem of the pulverization on the basis of the 2nd phase is not avoided, either.

[0018] The oxidation resistance of a hydrogen storing metal alloy is also an important property. If left by the hydrogen storing metal alloy in the atmosphere, a front face will oxidize and an oxide film will be formed. Especially as for V content alloy, an oxide film is easy to be formed. This oxide film cannot serve as an obstacle of hydrogen absorption, and cannot demonstrate predetermined hydrogen-absorption capacity. Therefore, in order that hydrogen storing metal alloy powder may remove an oxide film before use, activation is needed in many cases. This activation puts the end of an alloy powder into a proof-pressure container, is performed by carrying out the object for intercropping of the high-pressure hydrogen gas of dozens kg/cm<sup>2</sup> several one day - days at an elevated temperature, and requires costs for both a container and processing. Therefore, the hydrogen storing metal alloy powder which cannot oxidize easily even if it leaves it in air so that activation may become unnecessary is called for.

[0019] Although it is effective in oxidation-resistant improvement in hydrogen storing metal alloy powder, since metallic coating of the hydrogen storing metal alloy powder by electroless deposition given in JP,60-190570,A is what responded to this request and it is Cu and nickel in which a covering metal does not have hydrogen-absorption capacity at all, only in the part of a covering metal, hydrogen storage capacity decreases.

[0020] this invention is repeat hydrogen absorption / discharge life over a long period of time that it has high hydrogen-absorption capacity applicable to the use of storage and transportation of hydrogen gas, refining and separation of hydrogen gas, a heat transport and a cooling system, a hydrogen compressor, etc., and is hard to carry out pulverization. (endurance) It excels and is comparatively low (150 degrees C or less). Even if you can use it at temperature and you leave it in the atmosphere, let the thing with little degradation of a hydrogen-absorption property for which a comparatively cheap hydrogen storing metal alloy

[0021]

[Means for Solving the Problem] For this invention persons, the small Ti-Cr-V system hydrogen storing metal alloy of the diameter of crystal grain manufactured by the rapid solidification method is [ high hydrogen-absorption capacity and ] outstanding repeat hydrogen absorption / discharge life. (endurance) It had and the thing near the room temperature which can be comparatively used at low temperature was found out previously.

[0022] This hydrogen storing metal alloy is H/M (ratio of the number of hydrogen atoms to the composition atomic number which constitutes an alloy by which occlusion was carried out). 1.5 It is a maximum of 1.7 above. Maximum hydrogen storage capacity on the theory of the body-centered cubic lattice metal still represented by V although the high hydrogen storage capacity of a base is shown (H/M=2) When compared, it was still somewhat low, and room to increase hydrogen storage capacity further remained. When other little elements were added to the above-mentioned alloy composition as a result of subsequent research, it turns out that hydrogen storage capacity increases further, and this invention was reached.

[0023] this invention is formula:  $Ti_a V_1-a-b-c-d Cr_b Ac B_d$ . It is the hydrogen storing metal alloy which has the composition expressed and is characterized by the diameter of average crystal grain of the main phase being 40 micrometers or less. In the upper formula A Mn, Fe, Co, Cu, Nb, Zn, Zr, One sort or two sorts or more of elements chosen from Mo, Ag, Hf, Ta, W, aluminum, Si, C, N, P, and B are meant. B is Ln (lanthanoids system metal). And one sort or two sorts or more of elements chosen from Y are meant. The value of a is 0.2. It is 0.5 above. The value of the following and b is 0.1. It is 0.4 above. The value of the following and c is 0.01 or more and 0.2. The value of the following and d is 0.001. It is 0.03 or less above.

[0024] The small hydrogen storing metal alloy of this diameter of crystal grain can be manufactured by the rapid solidification method. In the suitable mode of this invention, it has nickel addition layer to which a hydrogen storing metal alloy makes a Ti-nickel compound a subject on a front face. the front face of a hydrogen storing metal alloy which manufactured this nickel addition layer by \*\* rapid solidification method -- nickel -- covering -- subsequently -- or it heat-treats at the temperature of 400-1000 degrees C -- or \*\* -- it can form by the mechanical alloying method covering the front face of this hydrogen storing metal alloy with nickel

[0025]

[Embodiments of the Invention] Hereafter, the hydrogen storing metal alloy and its manufacture method of this invention are explained in detail. The feature of the hydrogen storing metal alloy of this invention is (1).  $Ti_a V_1-a-b-c-d Cr_b Ac B_d$  (the inside of \*\* formula and a formula, and A, B and a-d are the same as the above) The chemical composition shown and (2) The diameters of average crystal grain of the main phase are 40 micrometers or less and two points of being detailed.

[0026] The main phase of this hydrogen storing metal alloy is a body center cubic, this crystal lattice consists of three elements of Ti, V, and Cr, and the part is the solid solution replaced by A element. Above (2) The detailed diameter of average crystal grain of the main phase is obtained by manufacturing a hydrogen storing metal alloy by rapid solidification methods, such as a chill roll method and the gas atomizing method. Therefore, it can be said that

the hydrogen storing metal alloy of this invention is "an alloy with the chemical composition shown by the above-mentioned \*\* formula by which rapid solidification was carried out." For example, if the cooling rate at the time of solidification becomes slow like an arc solution process, since crystal grain will grow and it will become big and rough during solidification, the diameter of average crystal grain of the main phase exceeds 40 micrometers.

[0027] The hydrogen storing metal alloy of this invention has high hydrogen-absorption capacity, and it excels in endurance that it is hard to carry out pulverization, and is [ near the room temperature ] comparatively low (150 degrees C or less). The reason which can be used at temperature is guessed as follows.

[0028] The Ti-V-Cr system alloy of a body center cubic which carried out rapid solidification as this invention persons found out previously is 0.1 MPa near atmospheric pressure. Hydrogen equilibrium pressure (balanced gas \*\* of hydrogen absorption and release reaction) Since the shown temperature can be as low as below 150 \*\*, and a lot of [ the temperature requirement below 150 \*\* ] hydrogen can be absorbed and it is hard to carry out pulverization, it excels in repeat hydrogen absorption / discharge life.

[0029] However, this high hydrogen storage capacity or outstanding endurance are not acquired like an arc solution process with the alloy with which the solidification after the dissolution was manufactured by the late conventional method. This is TiCr<sub>2</sub> with little hydrogen storage capacity, when the cooling rate at the time of solidification falls. The 2nd phase made into a subject is because it deposits at a remarkable rate during solidification. It is made easy to happen pulverization, since the sludge of this 2nd phase makes impossible reversible discharge of the hydrogen which it reduced hydrogen equilibrium pressure and it not only reduces hydrogen storage capacity, but absorbed it and serves as an origin of an intergranular fracture further. If it puts in another way, since there are very few amounts of deposits of this 2nd phase, in the hydrogen storing metal alloy of this invention, the fall and pulverization of hydrogen storage capacity resulting from this phase are avoidable.

[0030] According to this invention, hydrogen storage capacity can be increased further, maintaining a former alloy and the property which absorbs and emits hydrogen gas by temperature and the pressure mostly, and also suppressing formation of the 2nd phase of the above by adding the element shown in the Ti-V-Cr system alloy by which rapid solidification was carried out by A and B of the above-mentioned \*\* formula. The reason is considered as follows, although not necessarily solved completely.

[0031] A element (Mn, Fe, Co, Cu, Nb, Zn, Zr, Mo, Ag, Hf, Ta, W, aluminum, Si, C, N, P, B) It is replacing by Ti, V, and Cr which constitute the body center cubic of the main phase, and expanding a grid size, and it is expected that the hydrogen storage capacity of the alloy itself is raised. If these elements also have a slow cooling rate after the dissolution, it will be easy to form an intermetallic compound with Ti or Cr, carbide, and a boride, and hydrogen storage capacity will fall. Therefore, in order to obtain high hydrogen storage capacity and to suppress crystallization or a deposit of such a compound, it is necessary to carry out rapid solidification. Thereby, the pulverization from which this compound serves as an origin is also suppressed.

[0032] B element (a lanthanoids system metal <Ln> or Y) It is thought that it hardly exists in the body center cubic of the main phase, but the impurity oxygen and the oxide which are contained in an alloy are formed, and it exists. Although impurity oxygen exists in the state of invading between the metal atoms of the body center cubic of the main phase, the position upon which these elements trespass is also a position upon which a hydrogen atom trespasses, when occlusion of the hydrogen is carried out. Therefore, this impurity oxygen becomes the cause of decreasing hydrogen storage capacity in order to take up a hydrogen invasion site. If Ln and Y which are easy to combine with oxygen are added, impurity oxygen will be driven away out of the main phase, and what hydrogen storage capacity increases will be presumed.

[0033] The atomic ratio of each element of the hydrogen storing metal alloy of this invention was examined so that high hydrogen storage capacity might be obtained the low temperature below 150 \*\*, and near the atmospheric pressure, and it was determined as mentioned above. Next, the reason is explained. In addition, as shown in the above-mentioned \*\* formula, each amount of each element is an atomic ratio, and the sum total is 1.

[0034] Titanium If the amount of (Ti) Ti increases, the grid size of a body center cubic which is the alloy main phase will be expanded, and hydrogen storage capacity will increase. It is 0.2 in order to obtain high hydrogen storage capacity. If the above Ti is required and there are few amounts of Ti than this, hydrogen storage capacity will become low. Although hydrogen storage capacity increases, hydrogen equilibrium pressure falls in connection with it, and it becomes impossible to use it near a room temperature and the atmospheric pressure, so that there is much titanium.

[0035] Even if it adds Cr, it becomes impossible to raise hydrogen equilibrium pressure to near the atmospheric pressure, if the amount of Ti exceeds 0.5, although Cr is added in this invention as an element which raises hydrogen equilibrium pressure. Moreover, life [ as opposed to repeat hydrogen absorption and discharge of a cause in pulverization ] when there are too many amounts of Ti (endurance) It falls. The viewpoint of the balance of

endurance to hydrogen storage capacity and amount of Ti 0.2 or more and 0.5 It considers as the following and is 0.3 preferably. It is 0.3 more preferably 0.45 or less above. It is 0.4 above. It is the following.

[0036] Chromium Although hydrogen storage capacity will increase if the amount of (Cr) Cr(s) increases, since it is not so large as Ti the extent, the key objective of Cr addition is in control of hydrogen equilibrium pressure. Therefore, the amount of Cr(s) changes with the service temperatures and hydrogen equilibrium pressure which are made into the amount of Ti, or the purpose. However, the amount of Cr(s) is 0.1. At the following, the amount of Ti is 0.2. The hydrogen equilibrium pressure in a room temperature becomes quite lower than atmospheric pressure at a case, and it becomes impossible to be unable to absorb hydrogen and to emit it in reversible, near the room temperature.

[0037] On the other hand, Cr is 0.4. TiCr<sub>2</sub> which deposits as the 2nd phase if it exceeds The amount of a phase increases; not only hydrogen storage capacity falls, but pulverization becomes easy to happen and the life over hydrogen absorption and discharge falls repeatedly. The viewpoint of the balance of endurance to hydrogen storage capacity and amount of Cr(s) 0.1 or more and 0.4 It considers as the following and is 0.2 preferably. It is 0.4 above. It is 0.2 more preferably hereafter. It is 0.35 or less above.

[0038] Vanadium At the 2 yuan system of (V) Ti-Cr, it is TiCr<sub>2</sub> as the 2nd phase. It forms mostly, and a life [ repeatedly as opposed to hydrogen absorption and discharge with hydrogen storage capacity ] falls, hydrogen equilibrium pressure is too low and use near the room temperature also becomes difficult. Therefore, V is added together. Many body center cubic phases of the main phase are obtained by addition of V, and hydrogen storage capacity increases. The amount of V is automatically determined by the amount of Ti, Cr, A element, and B element.

[0039] A element (Mn, Fe, Co, Cu, Nb, Zn, Zr, Mo, Ag, Hf, Ta, W, aluminum, Si, C, N, P, B) These alloying elements are elements effective for replacing by Ti, Cr, or V that is the metal which constitutes the body center cubic of the main phase, expanding a grid size, and making hydrogen storage capacity increase.

[0040] Since these elements tend to form Ti or Cr, an intermetallic compound, carbide, and a boride, they can seldom be added in a large quantity, so that it may be expected from each 2 yuan system state diagram. The amount of A element is 0.2. If it increases, there is little hydrogen storage capacity, or since many compounds, such as the above-mentioned intermetallic compound which does not carry out occlusion of the hydrogen, are formed, the hydrogen storage capacity of the whole alloy will decrease on the contrary. On the other hand, if there are few amounts of A element than 0.01, the increase in the hydrogen storage capacity by addition will not be accepted.

[0041] The amount of the balance of the amounts of formation, such as an intermetallic compound, and hydrogen storage capacity to A element is 0.01 or more and 0.2. It considers as the following and is 0.05 or more and 0.15 or less more preferably 0.15 or less 0.03 or more.

[0042] B element [Ln (lanthanoids system metallic element) and Y] -- these alloying elements are added in order to make the impurity oxygen and the compound which exist in the hydrogen invasion site of the main phase of an alloy form Therefore, the amount of B element is influenced by the amount of impurity oxygen in an alloy. A few amount is enough, if a raw material with few impurities is used, although it is necessary to add mostly and is expensive, if a raw material with many impurities is used, although it is cheap at the time of alloy manufacture.

[0043] If use of a scrap etc. is taken into consideration although the amount of impurity oxygen of an alloy is usually less than [ 1wt% ] even if it uses a cheaply available raw material industrially, going up to more than 2wt% will also be considered. Generally Ln and Y are [ oxygen and ] B-2 O<sub>3</sub>. In order to form the oxide of type, it is enough if equivalent amount grade addition is carried out by impurity oxygen and the atomic ratio. Therefore, the upper limit of the amount of B element was set to 0.03. Even if it adds B element in a large quantity from this, it leads to cost increase only by increasing superfluous Ln which does not have big influence on a hydrogen-absorption property, and Y.

[0044] On the other hand, the amount of B element is 0.001. Below, impurity oxygen cannot be removed and hydrogen storage capacity does not increase. As mentioned above, it is the amount of B element 0.001 Although carried out to 0.03 or less above, this amount is made to fluctuate within the limits of this with the amount of impurity oxygen of an alloy, therefore the purity of a raw material to be used, as explained above.

[0045] Thus, since there are very few additions of expensive B element, the cost increase by the addition is slight. Moreover, although B element forms an oxide by the grain boundary of the main phase, since the amount is few as mentioned above, the bad influence of the hydrogen storage capacity by it decreases compared with increase of the hydrogen storage capacity by addition of this oxide. Moreover, since these oxides have the effect of suppressing big and rough-ization of the grain size number under heat treatment, they can make the upper limit of the heat treatment temperature which can obtain a fine crystal organization higher than the case of a Ti-V-Cr alloy by B element addition. Therefore, heat treatment time becomes short.

[0046] If the alloy called cheap misch metal which is the alloy of the rare earth metal and contains many lanthanoids system metals although it is also possible for a lanthanoids system metal to carry out independent addition of the elements refined as a pure metal, such as La and Ce, is used, the manufacturing cost of the hydrogen storing metal alloy of this invention will fall further.

[0047] As explained more than the diameter of average crystal grain of the main phase, the hydrogen storing metal alloy of this invention succeeds in adding two kinds of elements, A and B, into the Ti-Cr-V system alloy which makes the main phase a body center cubic with much [ from the first ] hydrogen storage capacity, and increasing hydrogen storage capacity further.

[0048] However, it is the solidification speed after the hydrogen storage capacity of this alloy changing with the diameters of average crystal grain of the manufacture method or the main phase even if it has the chemical composition of this Ti-Cr-V-A-B system, and dissolving at the time of alloy manufacture. (cooling rate) When it became late and the diameter of average crystal grain of the main phase exceeded 40 micrometers, even if it was the same composition, it became clear that hydrogen storage capacity falls.

[0049] This is TiCr<sub>2</sub> when solidification speed falls. In order that this sludge may have little hydrogen storage capacity of itself or may not carry out occlusion of the hydrogen, when the amount of sludges, such as an intermetallic compound with A element mentioned above, carbide, and a boride, increases, and its amount of the increases, the hydrogen storage capacity as the whole alloy is for falling.

[0050] Moreover, TiCr<sub>2</sub> If the amount of other sludges increases, since Ti in the alloy phase of a body center cubic which is the main phase, and the amount of Cr(s) will fall, it originates mainly in the amount reduction of Cr(s), the hydrogen equilibrium pressure which is balanced gas \*\* of hydrogen absorption and release reaction falls the hydrogen storage capacity of the main phase not only decreases, but, and it becomes impossible to emit the hydrogen absorbed in reversible.

[0051] Furthermore, pulverization when carrying out repeat hydrogen absorption / discharge examination, when the solidification speed at the time of alloy manufacture became slow and the diameter of average crystal grain of the main phase exceeded 40 micrometers (it can judge by the fall of a powder mean particle diameter) It becomes remarkable and is an alloy life. (endurance) The remarkable thing also made the fall clear. The main factor of this pulverization is above TiCr<sub>2</sub>. It is presumed that it is an intergranular fracture on the basis of sludges, such as an intermetallic compound with A element. Therefore, if solidification speed becomes slow and the amount of such a sludge increases, the origin of pulverization will increase and pulverization will become easy to happen.

[0052] At the hydrogen storing metal alloy of the above knowledge to this invention, it is the main phase. (body center cubic) The diameter of average crystal grain is limited to 40 micrometers or less. Thereby, it is TiCr<sub>2</sub>. In order that the amount of generation of sludges, such as an intermetallic compound with A element, may decrease remarkably, hydrogen storage capacity increases and the alloy in which the high hydrogen storage capacity beyond H/M=1.80 approaching the maximum hydrogen storage capacity on the theory of a body center cubic metal is shown is obtained. MnNi<sub>5</sub> which the pulverization at the time of hydrogen absorption and discharge stops being able to happen easily repeatedly simultaneously, and is a typical rare earth system hydrogen storing metal alloy The endurance excellent more remarkably than a system intermetallic compound over hydrogen absorption and discharge comes to be shown repeatedly.

[0053] In order to improve further these properties of the hydrogen storing metal alloy of this invention, it is desirable that 20 micrometers or less of diameters of average crystal grain of the main phase are especially 15 micrometers or less. Moreover, TiCr<sub>2</sub> formed as the 2nd phase It was it hard coming to generate pulverization that the diameter of average crystal grain of sludges, such as an intermetallic compound with A element, was 5 micrometers or less, and it became clear to hardly carry out pulverization to it being 2 micrometers or less.

[0054] The diameter of average crystal grain of the main phase can manufacture the hydrogen storing metal alloy of this invention 40 micrometers or less by the rapid solidification method, as mentioned above. The method of concrete rapid solidification is not limited as long as an alloy with the above-mentioned diameter of average crystal grain is obtained. As an employable rapid solidification method, it is the method of carrying out teeming of the alloy molten metal on a rotational electrode process, a rotating drum, or a roll. (an example, a single roll, or congruence chill roll method) A method, the gas atomizing method, etc. which are thinly cast to up to a water-cooled copper plate are mentioned.

[0055] A rotational electrode process and the atomizing method have [ among these ] a powder configuration advantageous at the point that pack density becomes high in a globular form substantially, when the trituration process for being able to manufacture the spherical-powder end of a hydrogen storing metal alloy, and carrying out the pulverization becomes unnecessary. In the case of other methods, the hydrogen storing metal alloy obtained if needed is ground, and it is made powder. As the trituration method, both hydrogenation trituration and machine

trituration can be adopted and both may be used together.

[0056] It is appropriate for the hydrogen storing metal alloy of this invention to consider as the powder gestalt whose mean particle diameter is about 10-50 micrometers. Thereby, a surface area increases and absorption and release reaction of hydrogen are promoted. If required, a classification will adjust a mean particle diameter.

[0057] The hydrogen storing metal alloy of this invention manufactured by the rapid solidification method has a minute quenching distortion. This quenching distortion is the endurance of the hydrogen storing metal alloy of this invention. (pulverization) Although not generated, especially a remarkable bad influence may heat-treat a hydrogen storing metal alloy by request, and may remove this quenching distortion. As for this heat treatment, it is desirable to carry out in a vacuum or inert gas in order to prevent oxidization of an alloy.

[0058] It is necessary to set up heat treatment conditions so that there may be no bird clapper during heat treatment more greatly [ the diameter of average crystal grain of the alloy main phase ] than 40 micrometers. This condition is usually temperature, although it changes also with diameters of average crystal grain of the main phase of the hydrogen storing metal alloy manufactured by the rapid solidification method. It is within the limits of 400-1000 degree-Cx 1 - 20 hours. However, when heat treatment temperature is as high as for example, more than 900 \*\*, heat treatment time is shortened and it is made for the diameter of average crystal grain of the alloy main phase after heat treatment not to exceed 40 micrometers. Since the heat treatment temperature of a Ti-V-Cr alloy is generally below 750 \*\*, the upper limit of heat treatment temperature can be made high by addition of B element.

[0059] When forming in an alloy front face nickel addition layer which makes a Ti-nickel compound a subject in order to raise the oxidation resistance of the hydrogen storing metal alloy of this invention so that it may mention later, it may heat-treat by the morphosis of this layer, and quenching distortion is also removed during this heat treatment. Therefore, heat treatment of only the purpose of removal of the quenching distortion in that case is unnecessary.

[0060] The hydrogen storing metal alloy of this invention is the low temperature near the room temperature, when it is left in the atmosphere. (an example, 80 degrees C) The measured hydrogen absorbed dose may decrease. That is, if this alloy is left in the atmosphere, a front face will oxidize, and this oxide film is considered that it becomes an obstacle and the hydrogen storage capacity in low temperature decreases. Thus, the hydrogen storing metal alloy to which hydrogen storage capacity fell by air neglect is among high-pressure hydrogen gas. (an example, 20 atmospheric pressure) If you make it heated and activated to 500 \*\*, the hydrogen absorbed dose will increase and the absorbed dose before neglect will be recovered. However, as mentioned above, this activation requires costs.

[0061] It is desirable to improve the oxidation resistance of the hydrogen storing metal alloy of this invention so that it may not oxidize, even if it contacts the atmosphere, in order to avoid the above-mentioned activation with the equipment using the hydrogen storing metal alloy, since contact to the atmosphere is completely unavoidable in manufacture process.

[0062] As a result of examining this point, when the front face of the hydrogen storing metal alloy of this invention was covered with nickel like the publication to JP,60-190570,A, it became clear that the oxidation resistance of an alloy is improved. However, although this technique is effective in oxidation-resistant improvement, since the nickel itself which covered the alloy front face does not almost have hydrogen-absorption capacity, the hydrogen absorbed dose per alloy unit weight falls.

[0063] Then, when changed into nickel addition layer which nickel enveloping layer on the front face of an alloy is made to react with the Ti-V-Cr-A-B system alloy used as a base material as a result of inquiring further, and makes a Ti-nickel compound a subject, since this nickel addition layer has bigger hydrogen-absorption capacity than pure nickel, it turns out that oxidation resistance can be given to a hydrogen storing metal alloy, without reducing most hydrogen absorbed dose. Therefore, in the suitable mode, the hydrogen storing metal alloy of this invention has nickel addition layer which makes a Ti-nickel compound a subject on the alloy front face. Oxidation resistance improves by that cause, without reducing hydrogen storage capacity substantially, and the activation mentioned above becomes unnecessary, or it is mitigated very much.

[0064] The covering method of nickel on the front face of an alloy is a physical method. (the method equivalent to the mechanical alloying mixed with an example, the method of mixing nickel impalpable powder and the end of an alloy powder, a ball mill, etc. is also included) Chemical method (an example, electrolysis nickel plating, non-electrolyzed nickel plating) Any are sufficient and there is especially no limit. Although the amount of covering of nickel changes also with powder mean particle diameters of a hydrogen storing metal alloy, 5 - 10 % of the weight is usually preferably suitable for it one to 20% of the weight to a hydrogen storing metal alloy. As long as it is required before this nickel covering, pickling processing of the hydrogen storing metal alloy may be carried out from the acid of non-oxidizing qualities, such as fluoric acid and a hydrochloric acid, and the oxidizing zone on the front face of an alloy may be removed.



[0065] After covering the front face of a hydrogen storing metal alloy with nickel, nickel addition layer which makes a Ti-nickel compound a subject is formed in a front face by heat-treating, making Ti component in a base material alloy nickel in surface coating react, and changing nickel layer to the high Ti-nickel compound of hydrogen-absorption capacity. Since this nickel addition layer has incorporated Cr from the base material, it excels the 2 yuan system intermetallic compound of Ti-nickel in oxidation resistance.

[0066] It is desirable to also perform this heat treatment in a vacuum or inert gas in order to prevent oxidization of an alloy. Heat treatment conditions are set up so that it will not change big and rough, by the time the diameter of average crystal grain of the main phase of a base material alloy exceeds 40 micrometers during this heat treatment. This viewpoint to heat treatment temperature It considers as the range of 400-1000 degrees C, and heat treatment time is set up so that the above-mentioned big and rough-ization may not take place. If heat treatment temperature exceeds 1000 degrees C, big and rough-ization of the sludge of the 2nd phase progresses, and the hydrogen absorbed dose will fall or it will become easy to carry out pulverization of the diameter of average crystal grain to hydrogen absorption and discharge by the repeat. On the other hand, the generation reaction of a Ti-nickel compound cannot progress easily under by 400 \*\*. Desirable heat treatment temperature It is 450-900 \*\*.

[0067] However, it is a long time for example, in a ball mill about nickel covering. (an example and 100 - 1000 hours) Since it is nickel addition layer which generated nickel covering already reacts with Ti in a base material alloy, and makes a Ti-nickel compound a subject when it carries out by the mechanical alloying method for carrying out, it is not necessary to heat-treat for a reaction.

[0068]

[Example] In production of an examination alloy, it is a RF solution process. (5 kg/ch) Button arc solution process (button size : 250 g/ch and 50 g/ch) Single chill roll method which used the copper roll (20 g/ch) The Ar gas atomizing method (10 g/ch) Or rotational electrode process (500 g/ch) It used. The raw material used for manufacture of an alloy molten metal is a misch metal which is the alloy of a purity 99wt% titanium sponge, a purity 98wt% vanadium, purity 99wt% chromium, and the lanthanoids system rare earth metal. . (It is written as Ln) It was purity 99wt% Fe, Mn, Co, Nb, Y, Zn and Zr, and purity 99.9wt% aluminum, Ag, Hf, Ta, W, Mo, and Cu (total La=46wt% and Ce=5wt% and Nd=37wt% and Pr=10wt% and rare earth content 99.5wt%). Light element (Si, C, N, P, B) Compound with Ti or Cr (TiC, TiB<sub>2</sub> grade) It added.

[0069] They are 300 \*\* and 2.5 MPa about the alloy obtained by methods other than the gas atomizing method powder is obtained directly, and a rotational electrode process. After hydrogenating in hydrogen gas for 5 hours, it ground mechanically, and it was made powder. Any end of an alloy powder is 100. The powder below mum was sorted out and used with the sieve. About a part of gas atomization material, in order to enlarge the diameter of average crystal grain, it heat-treated in argon atmosphere. The characterization method of an examination alloy is explained below collectively.

[0070] Hydrogen gas absorption, emission characteristic hydrogen gas absorption, and the emission characteristic were measured by the activation zero method using G BERUTSU type equipment. Measurement is 3.0MPa after putting in and carrying out evacuation of the examination alloy to a container and determining a zero. Under hydrogen pressure It carried out, after heating and carrying out activation to 300 - 500 \*\*. In order to remove the influence of oxidization of a front face in the end of an alloy powder in mechanical trituration, it is a 5vol% hydrofluoric acid about an examination alloy before activation. (fluoric acid) Pickling was carried out in solution.

[0071] the hydrogen-desorption-absorption cycle used for measurement -- the temperature of 80 degrees C -- it is -- hydrogen pressure -- 3.0 MPa from -- the hydrogen gas discharge lowered to 0.01 MPa, and hydrogen pressure -- 0.01 MPa to 3.0 MPa up to -- it consists of hydrogen gas absorption to pressurize

[0072] Hydrogen storage capacity produces a hydrogen-desorption curve at the time of hydrogen gas discharge of 1 cycle eye, and is pressure 1MPa. The value of hydrogen storage capacity was calculated and it evaluated by converting this amount of hydrogen into H/M which is the ratio of the absorbed number of hydrogen atoms to the metal atomic number which constitutes an alloy. H/M considered 1.80 or more as success.

[0073] The influence of the pulverization by the pulverization repeat hydrogen absorption and discharge by repeat hydrogen absorption and discharge is the aforementioned hydrogen-desorption-absorption cycle 300 It measured and evaluated which powder with a particle size of 20 micrometers or less increased after cycle \*\*\*\*\*. The particle-size-distribution measuring device of a laser diffraction formula was used for the particle size analysis. Since the difference was in powdered particle size distribution by the manufacture method, evaluation computed the fines rate of increase compared to the amount on the basis of the particle weight 20 micrometers or less before an examination by the following formula, and evaluated it. It is success if the fines rate of increase is 15% or less.

[0074]

[Equation 1]

$$\text{微粉増加率(\%)} = \left[ \frac{A - B}{B} \right] \times 100$$

A=300 サイクル試験後の20 μm以下の粉末量。  
B=試験前の20 μm以下の粉末量。

[0075] After measurement of the diameter of crystal grain of the main phase of the diameter examination alloy of crystal grain embedded the alloy before trituration at the epoxy resin and ground it, it \*\*\*\*\*ed by the mixed acid of 0.4 vol% fluoric acid and a 1vol% nitric acid, was observed with the optical microscope, and it was performed, and the average of the measurement result of 20 crystal grain chosen at random was made into the diameter of average crystal grain. Since it was detailed, the particle size of the sludge of the 2nd phase is SEM (secondary electron microscope). It used and measured and the average was calculated like the top.

[0076] Oxidation-resistant evaluation of the hydrogen storing metal alloy which carried out nickel covering of the oxidation-resistant front face, and formed nickel addition layer, the constant temperature of the temperature of 25 degrees C, and 65% of humidity -- G BERUTSU [ after leaving it for one week in the air atmosphere of constant humidity ] type hydrogen absorption / discharge testing device -- using -- activation -- nothing -- 80 degrees C -- 3.0 MPa The absorption test of hydrogen gas was performed and the decreasing rate of the hydrogen storage capacity in comparison with the hydrogen storage capacity of the alloy before forming nickel addition layer was computed by the following formula. It is success if the decreasing rate of hydrogen storage capacity is 10% or less.

[0077]

[Equation 2]

$$\text{水素吸収量低下率(\%)} = \left[ \frac{C - D}{C} \right] \times 100$$

C=Ni被覆前に活性化処理して測定した水素吸蔵量  
D= 1週間放置後に70℃で測定した水素吸蔵量

[0078] (Example 1) this example is an example which alloy composition was changed and examined the performance of a hydrogen storing metal alloy. As a method of producing a hydrogen storing metal alloy, since only the rapid solidification method was adopted, each diameter of average crystal grain of the main phase was 40 micrometers or less, and many were 20 micrometers or less. The measurement result of the hydrogen storage capacity of each alloy and the fines rate of increase is shown in Table 1 with alloy composition and the producing method.

[0079]

[Table 1-1]



試験 No.	化 学 組 成					溶解方法	水素 吸蔵量 (H/M)	微粉 増加率 (%)	備 考
	Ti	V	Cr	A	B				
1	0.30	0.37	0.30	Mn:0.02	Ln:0.01	ガスライズ	1.81	8	本 発 明 例
2	0.30	0.29	0.30	Mn:0.10	Ln:0.01	"	1.84	9	
3	0.30	0.21	0.30	Mn:0.18	Ln:0.01	"	1.82	10	
4	0.30	0.37	0.30	Fe:0.02	Ln:0.01	"	1.81	9	
5	0.30	0.21	0.30	Fe:0.18	Ln:0.01	"	1.81	13	
6	0.30	0.37	0.30	Co:0.02	Ln:0.01	"	1.81	8	
7	0.30	0.21	0.30	Co:0.18	Ln:0.01	"	1.82	11	
8	0.30	0.37	0.30	Cu:0.02	Ln:0.01	"	1.81	10	
9	0.30	0.21	0.30	Cu:0.18	Ln:0.01	"	1.82	12	
10	0.30	0.37	0.30	Nb:0.02	Ln:0.01	"	1.82	8	
11	0.30	0.21	0.30	Nb:0.18	Ln:0.01	"	1.84	14	
12	0.30	0.37	0.30	Zr:0.02	Ln:0.01	"	1.81	8	
13	0.30	0.21	0.30	Zr:0.18	Ln:0.01	"	1.83	13	
14	0.30	0.37	0.30	Mo:0.02	Ln:0.01	"	1.81	9	
15	0.30	0.21	0.30	Mo:0.18	Ln:0.01	"	1.81	12	
16	0.30	0.37	0.30	Ta:0.02	Ln:0.01	"	1.82	8	
17	0.30	0.21	0.30	Ta:0.18	Ln:0.01	"	1.83	13	
18	0.30	0.37	0.30	Al:0.02	Ln:0.01	"	1.81	10	
19	0.30	0.21	0.30	Al:0.18	Ln:0.01	"	1.81	14	
20	0.30	0.37	0.30	Si:0.02	Ln:0.01	"	1.81	8	
22	0.30	0.21	0.30	Si:0.18	Ln:0.01	"	1.83	11	
23	0.30	0.29	0.30	Ag:0.10	Ln:0.01	"	1.82	8	
24	0.30	0.29	0.30	Hf:0.10	Ln:0.01	"	1.83	9	
25	0.30	0.29	0.30	W :0.10	Ln:0.01	"	1.81	12	
26	0.30	0.25	0.30	Mn:0.07 Fe:0.07	Ln:0.01	"	1.84	10	
27	0.30	0.25	0.30	Fe:0.07 Cu:0.07	Ln:0.01	"	1.84	11	
28	0.30	0.25	0.30	Co:0.07 Nb:0.07	Ln:0.01	"	1.85	11	
29	0.30	0.27	0.30	Mn:0.05 Hf:0.05 C :0.02	Ln:0.01	"	1.82	8	
30	0.30	0.27	0.30	Nb:0.05 W :0.05 N :0.02	Ln:0.01	"	1.83	9	
31	0.30	0.27	0.30	Zr:0.04 Si:0.04 P :0.04	Ln:0.01	"	1.82	11	
32	0.30	0.27	0.30	Zr:0.04 Mn:0.04 B :0.04	Ln:0.01	ガスライズ	1.84	10	

[0080]

[Table 1-2]

試験 No.	化 学 組 成					溶解方法	水素 吸蔵量 (H/M)	微粉 増加率 (%)	考
	Ti	V	Cr	A	B				
33	0.30	0.24	0.30	Mn:0.05 Fe:0.05 Cu:0.05	Ln:0.01	"	1.86	10	本 発 明
34	0.30	0.24	0.30	Fe:0.05 Co:0.05 Nb:0.05	Ln:0.01	"	1.86	10	
35	0.30	0.256	0.30	Fe:0.14	Ln:0.004	"	1.81	9	
36	0.30	0.235	0.30	Fe:0.14	Ln:0.025	"	1.82	9	
37	0.30	0.25	0.30	Fe:0.14	Ln:0.01	"	1.83	8	
38	0.30	0.25	0.30	Fe:0.14	Ln:0.01	0-1 急冷	1.83	8	
39	0.30	0.25	0.30	Fe:0.14	Ln:0.01	回転電極	1.83	10	
40	0.30	0.24	0.30	Fe:0.05 Co:0.05 Nb:0.05	Ln:0.01	0-1 急冷	1.85	10	
41	0.30	0.24	0.30	Fe:0.05 Co:0.05 Nb:0.05	Ln:0.01	回転電極	1.85	12	
42	0.25	0.40	0.20	Fe:0.14	Ln:0.01	0-1 急冷	1.81	8	例
43	0.48	0.10	0.38	Fe:0.03	Ln:0.01	"	1.84	13	
44	0.48	0.10	0.38	Fe:0.03	Y :0.01	"	1.85	11	
45	0.48	0.10	0.38	Fe:0.03	Ln:0.005 Y :0.005	"	1.85	10	
46	0.30	0.40	0.30	—	—	"	1.71	8	比 較
47	0.30	0.15	0.30	Mn:0.24	Ln:0.01	"	1.65	18	
48	0.30	0.15	0.30	Fe:0.24	Ln:0.01	"	1.52	20	
49	0.30	0.15	0.30	Co:0.24	Ln:0.01	"	1.55	17	
50	0.30	0.15	0.30	Cu:0.24	Ln:0.01	"	1.51	22	
51	0.30	0.15	0.30	Nb:0.24	Ln:0.01	"	1.45	18	
52	0.30	0.15	0.30	Mn:0.10 Fe:0.10 Cu:0.04	Ln:0.01	"	1.50	23	
53	0.30	0.15	0.30	Fe:0.10 Co:0.10 Nb:0.04	Ln:0.01	"	1.48	21	
54	0.30	0.225	0.30	Mn:0.14	Ln:0.035	"	1.66	8	例
55	0.16	0.57	0.12	Fe:0.14	Ln:0.01	"	0.85	12	
56	0.30	0.47	0.08	Fe:0.14	Ln:0.01	"	1.41	13	
57	0.60	0.13	0.12	Fe:0.14	Ln:0.01	"	1.52	20	
58	0.30	0.10	0.45	Fe:0.14	Ln:0.01	"	0.78	19	
59	0.30	0.16	0.30	Mn:0.24	—	"	1.76	18	
60	0.30	0.39	0.30	—	Ln:0.01	"	1.75	9	

[0081] As Table 1 shows, it is low temperature near [ of 80 degrees C ] the room temperature comparatively, and each hydrogen storing metal alloy whose alloy composition is within the limits of this invention is understood that H/M shows high hydrogen storage capacity called 1.80 or more, and the rate of pulverization by repeat hydrogen absorption / discharge examination is as low as 15% or less, and there is much hydrogen storage capacity also near the room temperature, and there is little degradation by repeat hydrogen absorption and discharge.

[0082] On the other hand, No.46 which did not add A and a B car element With the alloy, hydrogen storage capacity was low. No.59 which added only one element of A and B, and 60 Increase of hydrogen storage capacity was [ but ] inadequate. Simultaneously with the fall of hydrogen storage capacity, the rate of pulverization also increased with the alloy of No.47-53 which had too many additions of A element. No.54 which had too many additions of B element Hydrogen storage capacity fell with the alloy. Even when the addition of A and a B car element was suitable, when each of alloys of No.55-58 with the content of Ti, Cr, and V out of range [ this invention ] had low hydrogen storage capacity and there were too many Ti and amounts of Cr, the rate of pulverization became large.

[0083] (Example 2) this example is an example which considered the influence the diameter of average crystal grain of the main phase affects the performance of a hydrogen storing metal alloy about the hydrogen storing metal alloy from which the diameter of average crystal grain of the main phase produced by the various manufacture methods differs. The chemical composition of a hydrogen storing metal alloy is Ti=0.30, V= 0.24, Cr=0.30, A= 0.15 (Mn=0.04, Fe=0.03, Cu=0.03, aluminum=0.03, B= 0.05), and B= 0.01 (Ln=0.01). It considered as the same composition. In order to see the influence of the diameter of crystal grain, the examination alloy heat-treated after

gas atomization was also produced. A test result is shown in Table 2. [0084]

[Table 2]

試験 No.	溶 解 方 法	立方晶主相 の結晶粒径 ( $\mu\text{m}$ )	析出物の 結晶粒径 ( $\mu\text{m}$ )	水素 吸収量 (H/M)	微粉 増加率 (%)	備 考
1	ガスアトマイズ	16	0.6	1.86	10	本 発 明 例
2	ロール急冷	15	0.5	1.86	9	
3	回転電極	15	0.6	1.85	10	
4	ガスアトマイズ 熱処理: 680 °C×10hr	30	1.7	1.82	13	
5	ガスアトマイズ 熱処理: 950 °C×2 hr	35	2.1	1.84	15	
6	ボタンアーク溶解, 50g	48	4.5	1.60	21	比 較 例
7	ボタンアーク溶解, 250g	70	9.5	1.55	25	
8	高周波溶解, 5 kg	85	10.6	1.25	32	
9	ガスアトマイズ 熱処理: 900 °C×15hr	45	4.2	1.55	20	
10	ガスアトマイズ 熱処理: 1300°C×10hr	65	5.5	1.40	33	

[0085] If a hydrogen storing metal alloy is produced by the rapid solidification method as shown in Table 2, the alloy of a detailed organization 20 micrometers or less will be obtained for the diameter of average crystal grain of the main phase. Although the diameter of crystal grain became big and rough when the hydrogen storing metal alloy of this detailed organization was heat-treated, when the diameter of average crystal grain of the main phase was 40 micrometers or less, both the hydrogen absorbed dose and the fines rate of increase were success. About the diameter of average crystal grain, if it is 40 micrometers or less, there will be no bad influence to the hydrogen storage capacity and the fines rate of increase by heat treatment also at the hot heat treatment in the alloy of this invention 950 \*\* for a short time. However, the direction of an alloy 20 micrometers or less had the high-achieving diameter of average crystal grain which has not been heat-treated after rapid solidification, and the fines rate of increase became 10% or less the top where hydrogen storage capacity is also high.

[0086] Moreover, the desirable range of the suppression of pulverization especially of [ that the diameter of average crystal grain of the main phase is 40 micrometers or less ] 2 micrometers or less also understands 5 micrometers or less also of diameters of average crystal grain of the sludge of the 2nd phase to be also a bird clapper from Table 2.

[0087] On the other hand, as for the late button arc dissolution material and late RF dissolution material of solidification speed, the diameter of average crystal grain of the main phase exceeded 40 micrometers, and both hydrogen storage capacity and the fines rate of increase became a rejection. (No.6-8) . When gas atomization material was heat-treated and heat treatment conditions were set up so that the diameter of average crystal grain might exceed 40 micrometers, hydrogen storage capacity and the fines rate of increase both fell greatly too (No.9, 10).

[0088] (Example 3) this example illustrates the oxidation-resistant improvement in the hydrogen storing metal alloy at the time of forming in an alloy front face nickel addition layer which makes a Ti-nickel compound a subject. Each examined hydrogen storing metal alloy is the powder produced by the Ar gas atomizing method. The chemical composition of an alloy was taken as the same composition of Ti=0.30, V= 0.25, Cr=0.30, A= 0.14, and B= 0.01. (however, the element kind of A and B change) .

[0089] nickel covering of the hydrogen storing metal alloy powder for forming nickel addition layer adopted both the physical method and the chemical method. By the physical method, after blending this 10% of the weight to the end of an alloy powder using nickel impalpable powder with a particle size of about 1 micrometer, it mixed uniformly with the mortar or mixed with the ball mill for a long time. The chemical method formed about 10% of the weight of nickel plating layer in the front face in the end of an alloy powder using commercial non-electrolyzed nickel plating liquid. In addition, though natural, even if it performs electrolysis plating, same nickel plating layer can be formed.

[0090] After giving nickel covering by these methods, nickel addition layer which makes a Ti-nickel compound a subject was formed in the alloy front face by heat-treating in argon atmosphere, making nickel enveloping layer react with the end of an alloy powder, and alloying. However, with the method of covering nickel powder with a ball mill mechanically, it is this ball mill mixture 100 Since alloying of nickel covering by mechanical alloying had taken place by carrying out time and for a long time, heat treatment was not performed. Moreover, as an example of comparison, this heat treatment is not performed but it is only nickel covering. (non-electrolyzed nickel plating or mortar mixture) The test coupon carried out was also produced.

[0091] In this way, it investigated by measuring hydrogen storage capacity, without carrying out activation of the oxidation resistance of the hydrogen storing metal alloy powder produced by the gas atomizing method for having formed nickel content layer on the front face after the neglect for one week in the atmosphere of predetermined conditions as mentioned above. About a test result, it is the formation method of nickel addition layer. (an upper case is the nickel covering method and the lower berth is heat treatment conditions) Existence of formation of the diameter of average crystal grain of the main phase, and a Ti-nickel compound phase (it checks by the X diffraction) It is shown in Table 3.

[0092]

[Table 3]

試験 No.	化学組成 <sup>1)</sup>		作製方法	Ni含有相形成 上: Ni付着法 下: 熱処理	平均 結晶 粒径	Ti-Ni 化合物 相形成	吸蔵量 低下率 (%)	備 考
	A	B						
1	Mn:0.07 Fe:0.07	Ln:0.01	ガスアライズ	無電解めっき 680℃×10hr	27μm	有	7	本 発 明 例
2	Mn:0.07 Fe:0.07	Ln:0.01	"	Ni粉末混合 680℃×10hr	27μm	有	10	
3	Mn:0.07 Fe:0.07	Ln:0.01	"	Ni粉末混合 680℃×100hr	15μm	有	9	
4	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき 400℃×10hr	20μm	有	6	
5	Co:0.07 Nb:0.07	Y :0.01	"	無電解めっき 680℃×25hr	23μm	有	5	
6	Zr:0.07 Ta:0.07	Y :0.01	"	無電解めっき 680℃×25hr	32μm	有	9	
7	Fe:0.04 Ta:0.04 Al:0.03 Si:0.03	Ln:0.01	"	無電解めっき 680℃×10hr	25μm	有	7	
8	Mn:0.04 Al:0.04 C :0.03 B :0.03	Ln:0.01	"	無電解めっき 680℃×10hr	23μm	有	8	
9	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき 950℃×2 hr	33μm	有	7	比 較 例
10	Mn:0.07 Fe:0.07	Ln:0.01	ガスアライズ	なし	15μm	—	35	
11	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき	15μm	無	19	
12	Mn:0.07 Fe:0.07	Ln:0.01	"	Ni微粉末混合	15μm	無	24	
13	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき 900℃×10hr	42μm	有	22	

<sup>1)</sup> Ti=0.30、V=0.25、Cr=0.30、A=0.14、B=0.01

[0093] As shown in Table 3, nickel covering was given according to this invention, when nickel addition layer which makes a Ti-nickel compound a subject by making nickel covering of a parenthesis react with an alloy content was formed in the alloy front face, oxidization in the atmosphere of the hydrogen storing metal alloy of this invention was suppressed, and even if it measured hydrogen storage capacity, without carrying out activation after one-week neglect, the fall of hydrogen storage capacity was suppressed to 10% or less. That is, since a front face hardly oxidizes even if it deals with the powder of a hydrogen storing metal alloy in the atmosphere, the activation which handling becomes very easy and costs require does not have needlessness, and is mitigated.

[0094] On the other hand, in the example of comparison, when nickel covering was not given at all, the hydrogen absorbed dose of the alloy-powder end after one-week neglect fell no less than 35% (No.9). However, even if it gave nickel covering, when nickel covering was not made to react with an alloy content by heat treatment or mechanical alloying, the hydrogen absorbed dose of the alloy-powder end after one-week neglect fell no less than 19 to 24%. (No.10, 11). That is, compared with the case of not covering, it turns out only by nickel covering that oxidation-resistant improvement is remarkably few. Moreover, when the heat treatment conditions for the reaction after nickel covering were unsuitable and the diameter of average crystal grain of the main phase exceeded 40 micrometers, hydrogen storage capacity fell greatly too under the influence of big-and-rough-izing.

[0095]

[Effect of the Invention] Hydrogen storage capacity is very as high as more than  $H/M=1.80$ , and the hydrogen storing metal alloy of this invention is low temperature near the room temperature comparatively. (an example and below 150 \*\*) Since it is hard to carry out pulverization even if it is easy to use for various uses and repeats hydrogen absorption and discharge over a long period of time, since absorption and discharge of hydrogen take place, the high hydrogen absorbed dose is held for a long period of time. (surpass endurance) And it is comparatively cheap.

[0096] Moreover, if nickel addition layer which makes a Ti-nickel compound a subject is formed in an alloy front face, since the fall of the hydrogen absorbed dose when the oxidation resistance of an alloy improving remarkably and leaving it in the atmosphere will become very small, it becomes possible to deal with it easily in the atmosphere, and the activation which costs require becomes unnecessary, or it is mitigated. Therefore, the hydrogen storing metal alloy of this invention is the the best for uses, such as an object for hydrogen gas storage / transportation, an object for hydrogen gas separation / refining, a heat-transport system and a cooling system, and a static compressor.

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**TECHNICAL FIELD**

[The technical field to which invention belongs] this invention is the amount of hydrogen absorption. (hydrogen-absorption capacity) Highly and simultaneous, repeatedly, it is few, and property degradation by hydrogen absorption discharge can use at the temperature near the room temperature, and is related with the hydrogen storing metal alloy with the feature of being comparatively cheap excellent in endurance, and its manufacture method. The hydrogen storing metal alloy of this invention with these features is an object for hydrogen gas storage / transportation, and an object for hydrogen gas separation / refining, and especially the further is the the best for a heat-transport system, a cooling system, a static compressor, etc.

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**PRIOR ART**

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[Description of the Prior Art] If hydrogen gas burns, in order that it may become water and may form neither carbon dioxide gas nor a sulfur oxide like a fossil fuel, it is a clean energy source.

[0003] Generally storage and transportation of hydrogen gas are compressed, and is performed as a high pressure gas. The cold-storage container of -253 \*\* is required for storage of liquid hydrogen, and the top where an evaporation loss is also large, since a lot of energy is required for liquefaction of hydrogen, it liquefies like nitrogen and stores because it is difficult. However, it is volume although the proof-pressure container which is heavy and is bulky is required for high-pressure hydrogen gas. It does not become about 1/200, but when it is inefficient-like, there is a problem also in safety.

[0004] Then, using for storage and transportation of hydrogen gas the hydrogen storing metal alloy which can absorb and emit hydrogen gas in reversible by cooling and heating has been examined. The storage density of a hydrogen storing metal alloy of the hydrogen gas per unit volume is higher than a high-pressure hydrogen gas container, it becomes more nearly lightweight and the hydrogen gas storage container of a snug product, and transportation of hydrogen gas also becomes easy. Moreover, since it is low voltage, safety is high and strong also against the mechanical shock under transportation.

[0005] The hydrogen storing metal alloy aiming at storage and transportation of hydrogen is developed conventionally, and is already used for storage of small-scale hydrogen. Moreover, the research of a low-pollution hydrogen fueled car which uses hydrogen gas as an alternate fuel of a gasoline is also progressing, and various kinds of hydrogen storing metal alloys including a FeTi system are examined by this as a hydrogen storage device.

[0006] There is other the following in the use it is expected that utilization of a hydrogen storing metal alloy is. Absorption of the hydrogen of a hydrogen storing metal alloy (hydrogenation) Discharge (decomposition of a hydride) It is a reversible reaction accompanied by discharge and absorption of heat, and has a heat-chemical energy conversion function. It can be used for a cooling system using this function as storage and the space transportation system, and the chemical heat pump of heat energy.

[0007] Moreover, if the hydrogen storing metal alloy which made hydrogen gas absorb at low temperature is heated to an elevated temperature, high-pressure hydrogen gas will be emitted. The function in which this transforms heat energy into mechanical energy is also achieved. This function can be used as heat drive type a static hydrogen compressor and an actuator.

[0008] Absorption / discharge speed of the hydrogen gas of a hydrogen storing metal alloy is larger than absorption / discharge speed of other gas constituents, and has a difference also between hydrogen isotopes. Therefore, hydrogen separation of isotopes is possible for separation of the high grade hydrogen gas from mixed gas, refining of impure hydrogen gas, and a further by using a hydrogen storing metal alloy and making hydrogen or a specific hydrogen isotope absorb or emit alternatively.

[0009] Thus, although there is a broad use in a hydrogen storing metal alloy, hydrogen storage capacity is the most important property to every use. Moreover, since the above-mentioned use needs comparatively a lot of hydrogen storing metal alloys for all, even if it repeats and uses a hydrogen storing metal alloy, there are few depressions and it is important to excel in endurance and that the price of an alloy is also comparatively cheap. Depending on a use, it is the comparatively low temperature near the room temperature. (an example and below 150 \*\*) It is also called for that absorption and discharge of hydrogen take place.

[0010] For example, LaNi<sub>5</sub> which utilization preceded Or MmNi<sub>5</sub> AB<sub>5</sub> represented Since the hydrogen storing metal alloy of type is expensive, even if the amount of the hydrogen storing metal alloy used can use it for small rechargeable batteries, such as a few Ni-H battery, a price side to use is difficult for it for the use which needs a lot of hydrogen storing metal alloys called the object for hydrogen gas storage. Moreover, there is not so much hydrogen storage capacity.

[0011] To JP,59-38293,B, it is comparatively cheap, and the Ti-Cr-V system alloy is indicated as a hydrogen storing metal alloy with much hydrogen storage capacity. As the manufacture method of an alloy, only the arc process is explained concretely. The hydrogen storing metal alloy which consists of the same components also as JP,7-252560,A is indicated. The analogous hydrogen storing metal alloy of a Ti-V-nickel system is indicated by JP,7-268513,A and JP,7-268514,A.

[0012] Moreover, by covering copper and/or a nickel metal with wet electroless deposition to hydrogen storing metal alloy powder, influence of contamination by the impurity gas in atmosphere can be made small, and the thing with unnecessary initial-activity-izing which it is and can be mitigated by carrying out is explained to JP,60-190570,A.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] For the hydrogen storing metal alloy of this invention, it is very high and hydrogen storage capacity is [ more than  $H/M=1.80$  and ] the comparatively low temperature near the room temperature. (an example and below 150 \*\*) Since it is hard to carry out pulverization even if it is easy to use for various uses and repeats hydrogen absorption and discharge over a long period of time, since absorption and discharge of hydrogen take place, the high amount of hydrogen absorption is held for a long period of time. (surpass endurance) And it is comparatively cheap.

[0096] Moreover, if nickel addition layer which makes a Ti-nickel compound a subject is formed in an alloy front face, since the fall of the amount of hydrogen absorption when the oxidation resistance of an alloy improving remarkably and leaving it in the atmosphere will become very small, it becomes possible to deal with it easily in the atmosphere, and the activation which costs require becomes unnecessary, or it is mitigated. Therefore, the hydrogen storing metal alloy of this invention is the the best for uses, such as an object for hydrogen gas storage / transportation, an object for hydrogen gas separation / refining, a heat-transport system and a cooling system, and a static compressor.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] Absorption and discharge of the hydrogen gas of a hydrogen storing metal alloy are a chemical reaction accompanied by expansion and contraction of volume, respectively. In order to obtain a practical reaction rate, it needs to be powdered and it is necessary to use a hydrogen storing metal alloy and to increase a surface area. However, if expansion and contraction of the volume in the end of an alloy powder are repeated during use, a crack will go into powder by internal distortion, it will be soon divided into a fine particle, and powder will carry out pulverization. If pulverization advances, hydrogen gas will not flow easily by lock out, or fines will be mixed with the flow of hydrogen gas and will move into gas piping. Therefore, this pulverization is long-term repeat hydrogen absorption / discharge life of a hydrogen storing metal alloy. (namely, endurance) It becomes the big cause of a fall.

[0014] Although the Ti-Cr-V system hydrogen storing metal alloy and Ti-V-nickel system alloy which were mentioned above are developed as an alloy with much hydrogen storage capacity, predetermined hydrogen storage capacity is not reached in many cases in fact, and the problem of the endurance by the above-mentioned pulverization cannot be solved, either.

[0015] For example, when it manufactures by the arc process as indicated by this official report, since solidification speed is slow, a Ti-Cr-V system hydrogen storing metal alloy given in JP,59-38293,B is low TiCr<sub>2</sub> of hydrogen storage capacity as the 2nd phase. An intermetallic compound deposits at a remarkable rate and hydrogen storage capacity falls. Moreover, a crack enters with this 2nd phase as the starting point into the repeat of hydrogen absorption and discharge in the end of an alloy powder, and there is also a trouble that pulverization is promoted.

[0016] After it holds a hydrogen storing metal alloy given in JP,7-252560,A at the elevated temperature of 1200-1400 degrees C in order to reduce the 2nd above-mentioned phase, and it considers as a cubic single phase organization in the example, the process which quenches with water cooling immediately is taken. However, since big and rough-ization of crystal grain arises in the case of heating-at-high-temperature maintenance, even if the amount of deposits of the 2nd phase decreases, the intensity of the material itself becomes weak by big and rough-ization, and it becomes easy to carry out pulverization of it by this method. In case it moreover mass-produces industrially, in order to use a large-sized ingot, also with water cooling, sufficient cooling rate is not obtained, but the big and rough sludge of the 2nd phase which makes a Ti-Cr compound a subject is formed, and hydrogen storage capacity also falls.

[0017] A Ti-V-nickel system hydrogen storing metal alloy given in each official report of JP,7-268513,A and 7-268514 is the Ti Ni alloy phase of the 2nd phase, or AB<sub>2</sub> to the grain boundary of the host phase which consists of a Ti-V system alloy. A type RABESU alloy phase has the organization in which the 3-dimensional mesh frame was formed. In order that this grain-boundary phase may raise reactivity with the hydrogen of an alloy, even if a host phase has some oxidization, absorption and discharge of hydrogen gas are possible through this grain-boundary phase. However, in order to deposit the 2nd low phase of hydrogen-absorption capacity in a large quantity so that the 3-dimensional network structure is formed, the hydrogen quantity to be stored of the whole alloy falls. Moreover, the problem of the pulverization on the basis of the 2nd phase is not avoided, either.

[0018] The oxidation resistance of a hydrogen storing metal alloy is also an important property. If left by the hydrogen storing metal alloy in the atmosphere, a front face will oxidize and an oxide film will be formed. Especially as for V content alloy, an oxide film is easy to be formed. This oxide film cannot serve as an obstacle of hydrogen absorption, and cannot demonstrate predetermined hydrogen-absorption capacity. Therefore, in order that hydrogen storing metal alloy powder may remove an oxide film before use, activation is needed in many cases. This activation puts the end of an alloy powder into a proof-pressure container, is performed by carrying out the object for intercropping of the high-pressure hydrogen gas of dozens kg/cm<sup>2</sup> several one day - days at an elevated temperature, and requires costs for both a container and processing. Therefore, the hydrogen storing metal alloy

powder which cannot oxidize easily even if it leaves it in air so that activation may become unnecessary is called for.

[0019] Although it is effective in oxidation-resistant improvement in hydrogen storing metal alloy powder, since metallic coating of the hydrogen storing metal alloy powder by electroless deposition given in JP,60-190570,A is what responded to this request and it is Cu and nickel in which a covering metal does not have hydrogen-absorption capacity at all, only in the part of a covering metal, hydrogen storage capacity decreases.

[0020] this invention is repeat hydrogen absorption / discharge life over a long period of time that it has high hydrogen-absorption capacity applicable to the use of storage and transportation of hydrogen gas, refining and separation of hydrogen gas, a heat transport and a cooling system, a hydrogen compressor, etc., and is hard to carry out pulverization. (endurance) It excels and is comparatively low (150 degrees C or less). Even if you can use it at temperature and you leave it in the atmosphere, let the thing with little degradation of a hydrogen-absorption property for which a comparatively cheap hydrogen storing metal alloy

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MEANS

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[Means for Solving the Problem] For this invention persons, the small Ti-Cr-V system hydrogen storing metal alloy of the diameter of crystal grain manufactured by the rapid solidification method is [ high hydrogen-absorption capacity and ] outstanding repeat hydrogen absorption / discharge life. (endurance) It had and the thing near the room temperature which can be comparatively used at low temperature was found out previously.

[0022] This hydrogen storing metal alloy is H/M (ratio of the number of hydrogen atoms to the composition atomic number which constitutes an alloy by which occlusion was carried out). 1.5 It is a maximum of 1.7 above. Maximum hydrogen storage capacity on the theory of the body-centered cubic lattice metal still represented by V although the high hydrogen storage capacity of a base is shown (H/M=2) When compared, it was still somewhat low, and room to increase hydrogen storage capacity further remained. When other little elements were added to the above-mentioned alloy composition as a result of subsequent research, it turns out that hydrogen storage capacity increases further, and this invention was reached.

[0023] this invention is formula:  $Ti_a V_{1-a-b-c-d} Cr_b Ac B_d$ . It is the hydrogen storing metal alloy which has the composition expressed and is characterized by the diameter of average crystal grain of the main phase being 40 micrometers or less. In the upper formula A Mn, Fe, Co, Cu, Nb, Zn, Zr, One sort or two sorts or more of elements chosen from Mo, Ag, Hf, Ta, W, aluminum, Si, C, N, P, and B are meant. B is Ln (lanthanoids system metal). And one sort or two sorts or more of elements chosen from Y are meant. The value of a is 0.2. It is 0.5 above. The value of the following and b is 0.1. It is 0.4 above. The value of the following and c is 0.01 or more and 0.2. The value of the following and d is 0.001. It is 0.03 or less above.

[0024] The small hydrogen storing metal alloy of this diameter of crystal grain can be manufactured by the rapid solidification method. In the suitable mode of this invention, it has nickel addition layer to which a hydrogen storing metal alloy makes a Ti-nickel compound a subject on a front face. the front face of a hydrogen storing metal alloy which manufactured this nickel addition layer by \*\* rapid solidification method -- nickel -- covering -- subsequently -- or it heat-treats at the temperature of 400-1000 degrees C -- or \*\* -- it can form by the mechanical alloying method covering the front face of this hydrogen storing metal alloy with nickel

[0025]

[Embodiments of the Invention] Hereafter, the hydrogen storing metal alloy and its manufacture method of this invention are explained in detail. The feature of the hydrogen storing metal alloy of this invention is (1).  $Ti_a V_{1-a-b-c-d} Cr_b Ac B_d$  (the inside of \*\* formula and a formula, and A, B and a-d are the same as the above) The chemical composition shown and (2) The diameters of average crystal grain of the main phase are 40 micrometers or less and two points of being detailed.

[0026] The main phase of this hydrogen storing metal alloy is a body center cubic, this crystal lattice consists of three elements of Ti, V, and Cr, and the part is the solid solution replaced by A element. Above (2) The detailed diameter of average crystal grain of the main phase is obtained by manufacturing a hydrogen storing metal alloy by rapid solidification methods, such as a chill roll method and the gas atomizing method. Therefore, it can be said that the hydrogen storing metal alloy of this invention is "an alloy with the chemical composition shown by the above-mentioned \*\* formula by which rapid solidification was carried out." For example, if the cooling rate at the time of solidification becomes slow like an arc solution process, since crystal grain will grow and it will become big and rough during solidification, the diameter of average crystal grain of the main phase exceeds 40 micrometers.

[0027] The hydrogen storing metal alloy of this invention has high hydrogen-absorption capacity, and it excels in endurance that it is hard to carry out pulverization, and is [ near the room temperature ] comparatively low (150 degrees C or less). The reason which can be used at temperature is guessed as follows.

[0028] The Ti-V-Cr system alloy of a body center cubic which carried out rapid solidification as this invention persons found out previously is 0.1 MPa near atmospheric pressure. Hydrogen equilibrium pressure (balanced gas

\*\* of hydrogen absorption and release reaction) Since the shown temperature can be as low as below 150 \*\*, and a lot of [ the temperature requirement below 150 \*\* ] hydrogen can be absorbed and it is hard to carry out pulverization, it excels in repeat hydrogen absorption / discharge life.

[0029] However, this high hydrogen storage capacity or outstanding endurance are not acquired like an arc solution process with the alloy with which the solidification after the dissolution was manufactured by the late conventional method. This is TiCr<sub>2</sub> with little hydrogen storage capacity, when the cooling rate at the time of solidification falls. The 2nd phase made into a subject is because it deposits at a remarkable rate during solidification. It is made easy to happen pulverization, since the sludge of this 2nd phase makes impossible reversible discharge of the hydrogen which it reduced hydrogen equilibrium pressure and it not only reduces hydrogen storage capacity, but absorbed it and serves as an origin of an intergranular fracture further. If it puts in another way, since there are very few amounts of deposits of this 2nd phase, in the hydrogen storing metal alloy of this invention, the fall and pulverization of hydrogen storage capacity resulting from this phase are avoidable.

[0030] According to this invention, hydrogen storage capacity can be increased further, maintaining a former alloy and the property which absorbs and emits hydrogen gas by temperature and the pressure mostly, and also suppressing formation of the 2nd phase of the above by adding the element shown in the Ti-V-Cr system alloy by which rapid solidification was carried out by A and B of the above-mentioned \*\* formula. The reason is considered as follows, although not necessarily solved completely.

[0031] A element (Mn, Fe, Co, Cu, Nb, Zn, Zr, Mo, Ag, Hf, Ta, W, aluminum, Si, C, N, P, B) It is replacing by Ti, V, and Cr which constitute the body center cubic of the main phase, and expanding a grid size, and it is expected that the hydrogen storage capacity of the alloy itself is raised. If these elements also have a slow cooling rate after the dissolution, it will be easy to form an intermetallic compound with Ti or Cr, carbide, and a boride, and hydrogen storage capacity will fall. Therefore, in order to obtain high hydrogen storage capacity and to suppress crystallization or a deposit of such a compound, it is necessary to carry out rapid solidification. Thereby, the pulverization from which this compound serves as an origin is also suppressed.

[0032] B element (a lanthanoids system metal <Ln> or Y) It is thought that it hardly exists in the body center cubic of the main phase, but the impurity oxygen and the oxide which are contained in an alloy are formed, and it exists. Although impurity oxygen exists in the state of invading between the metal atoms of the body center cubic of the main phase, the position upon which these elements trespass is also a position upon which a hydrogen atom trespasses, when occlusion of the hydrogen is carried out. Therefore, this impurity oxygen becomes the cause of decreasing hydrogen storage capacity in order to take up a hydrogen invasion site. If Ln and Y which are easy to combine with oxygen are added, impurity oxygen will be driven away out of the main phase, and what hydrogen storage capacity increases will be presumed.

[0033] The atomic ratio of each element of the hydrogen storing metal alloy of this invention was examined so that high hydrogen storage capacity might be obtained the low temperature below 150 \*\*, and near the atmospheric pressure, and it was determined as mentioned above. Next, the reason is explained. In addition, as shown in the above-mentioned \*\* formula, each amount of each element is an atomic ratio, and the sum total is 1.

[0034] Titanium If the amount of (Ti) Ti increases, the grid size of a body center cubic which is the alloy main phase will be expanded, and hydrogen storage capacity will increase. It is 0.2 in order to obtain high hydrogen storage capacity. If the above Ti is required and there are few amounts of Ti than this, hydrogen storage capacity will become low. Although hydrogen storage capacity increases, hydrogen equilibrium pressure falls in connection with it, and it becomes impossible to use it near a room temperature and the atmospheric pressure, so that there is much titanium.

[0035] Even if it adds Cr, it becomes impossible to raise hydrogen equilibrium pressure to near the atmospheric pressure, if the amount of Ti exceeds 0.5, although Cr is added in this invention as an element which raises hydrogen equilibrium pressure. Moreover, life [ as opposed to repeat hydrogen absorption and discharge of a cause in pulverization ] when there are too many amounts of Ti (endurance) It falls. The viewpoint of the balance of endurance to hydrogen storage capacity and amount of Ti 0.2 or more and 0.5 It considers as the following and is 0.3 preferably. It is 0.3 more preferably 0.45 or less above. It is 0.4 above. It is the following.

[0036] Chromium Although hydrogen storage capacity will increase if the amount of (Cr) Cr(s) increases, since it is not so large as Ti the extent, the key objective of Cr addition is in control of hydrogen equilibrium pressure. Therefore, the amount of Cr(s) changes with the service temperatures and hydrogen equilibrium pressure which are made into the amount of Ti, or the purpose. However, the amount of Cr(s) is 0.1. At the following, the amount of Ti is 0.2. The hydrogen equilibrium pressure in a room temperature becomes quite lower than atmospheric pressure at a case, and it becomes impossible to be unable to absorb hydrogen and to emit it in reversible, near the room temperature.

[0037] On the other hand, Cr is 0.4. TiCr<sub>2</sub> which deposits as the 2nd phase if it exceeds The amount of a phase increases, not only hydrogen storage capacity falls, but pulverization becomes easy to happen and the life over hydrogen absorption and discharge falls repeatedly. The viewpoint of the balance of endurance to hydrogen storage capacity and amount of Cr(s) 0.1 or more and 0.4 It considers as the following and is 0.2 preferably. It is 0.4 above. It is 0.2 more preferably hereafter. It is 0.35 or less above.

[0038] Vanadium At the 2 yuan system of (V) Ti-Cr, it is TiCr<sub>2</sub> as the 2nd phase. It forms mostly, and a life [ repeatedly as opposed to hydrogen absorption and discharge with hydrogen storage capacity ] falls, hydrogen equilibrium pressure is too low and use near the room temperature also becomes difficult. Therefore, V is added together. Many body center cubic phases of the main phase are obtained by addition of V, and hydrogen storage capacity increases. The amount of V is automatically determined by the amount of Ti, Cr, A element, and B element.

[0039] A element (Mn, Fe, Co, Cu, Nb, Zn, Zr, Mo, Ag, Hf, Ta, W, aluminum, Si, C, N, P, B) These alloying elements are elements effective for replacing by Ti, Cr, or V that is the metal which constitutes the body center cubic of the main phase, expanding a grid size, and making hydrogen storage capacity increase.

[0040] Since these elements tend to form Ti or Cr, an intermetallic compound, carbide, and a boride, they can seldom be added in a large quantity, so that it may be expected from each 2 yuan system state diagram. The amount of A element is 0.2. If it increases, there is little hydrogen storage capacity, or since many compounds, such as the above-mentioned intermetallic compound which does not carry out occlusion of the hydrogen, are formed, the hydrogen storage capacity of the whole alloy will decrease on the contrary. On the other hand, if there are few amounts of A element than 0.01, the increase in the hydrogen storage capacity by addition will not be accepted.

[0041] The amount of the balance of the amounts of formation, such as an intermetallic compound, and hydrogen storage capacity to A element is 0.01 or more and 0.2. It considers as the following and is 0.05 or more and 0.15 or less more preferably 0.15 or less 0.03 or more.

[0042] B element [Ln (lanthanoids system metallic element) and Y] -- these alloying elements are added in order to make the impurity oxygen and the compound which exist in the hydrogen invasion site of the main phase of an alloy form Therefore, the amount of B element is influenced by the amount of impurity oxygen in an alloy. A few amount is enough, if a raw material with few impurities is used, although it is necessary to add mostly and is expensive, if a raw material with many impurities is used, although it is cheap at the time of alloy manufacture.

[0043] If use of a scrap etc. is taken into consideration although the amount of impurity oxygen of an alloy is usually less than [ 1wt% ] even if it uses a cheaply available raw material industrially, going up to more than 2wt% will also be considered. Generally Ln and Y are [ oxygen and ] B-2 O<sub>3</sub>. In order to form the oxide of type, it is enough if equivalent amount grade addition is carried out by impurity oxygen and the atomic ratio. Therefore, the upper limit of the amount of B element was set to 0.03. Even if it adds B element in a large quantity from this, it leads to cost increase only by increasing superfluous Ln which does not have big influence on a hydrogen-absorption property, and Y.

[0044] On the other hand, the amount of B element is 0.001. Below, impurity oxygen cannot be removed and hydrogen storage capacity does not increase. As mentioned above, it is the amount of B element 0.001 Although carried out to 0.03 or less above, this amount is made to fluctuate within the limits of this with the amount of impurity oxygen of an alloy, therefore the purity of a raw material to be used, as explained above.

[0045] Thus, since there are very few additions of expensive B element, the cost increase by the addition is slight. Moreover, although B element forms an oxide by the grain boundary of the main phase, since the amount is few as mentioned above, the bad influence of the hydrogen storage capacity by it decreases compared with increase of the hydrogen storage capacity by addition of this oxide. Moreover, since these oxides have the effect of suppressing big and rough-ization of the grain size number under heat treatment, they can make the upper limit of the heat treatment temperature which can obtain a fine crystal organization higher than the case of a Ti-V-Cr alloy by B element addition. Therefore, heat treatment time becomes short.

[0046] If the alloy called cheap misch metal which is the alloy of a rare earth metal and contains many lanthanoids system metals although it is also possible for a lanthanoids system metal to carry out independent addition of the elements refined as a pure metal, such as La and Ce, is used, the manufacturing cost of the hydrogen storing metal alloy of this invention will fall further.

[0047] As explained more than the diameter of average crystal grain of the main phase, the hydrogen storing metal alloy of this invention succeeds in adding two kinds of elements, A and B, into the Ti-Cr-V system alloy which makes the main phase a body center cubic with much [ from the first ] hydrogen storage capacity, and increasing hydrogen storage capacity further.

[0048] However, it is the solidification speed after the hydrogen storage capacity of this alloy changing with the

diameters of average crystal grain of the manufacture method or the main phase even if it has the chemical composition of this Ti-Cr-V-A-B system, and dissolving at the time of alloy manufacture. (cooling rate) When it became late and the diameter of average crystal grain of the main phase exceeded 40 micrometers, even if it was the same composition, it became clear that hydrogen storage capacity falls.

[0049] This is TiCr<sub>2</sub> when solidification speed falls. In order that this sludge may have little hydrogen storage capacity of itself or may not carry out occlusion of the hydrogen, when the amount of sludges, such as an intermetallic compound with A element mentioned above, carbide, and a boride, increases, and its amount of the increases, the hydrogen storage capacity as the whole alloy is for falling.

[0050] Moreover, TiCr<sub>2</sub> If the amount of other sludges increases, since Ti in the alloy phase of a body center cubic which is the main phase, and the amount of Cr(s) will fall, it originates mainly in the amount reduction of Cr(s), the hydrogen equilibrium pressure which is balanced gas \*\* of hydrogen absorption and release reaction falls the hydrogen storage capacity of the main phase not only decreases, but, and it becomes impossible to emit the hydrogen absorbed in reversible.

[0051] Furthermore, pulverization when carrying out repeat hydrogen absorption / discharge examination, when the solidification speed at the time of alloy manufacture became slow and the diameter of average crystal grain of the main phase exceeded 40 micrometers (it can judge by the fall of a powder mean particle diameter) It becomes remarkable and is an alloy life. (endurance) The remarkable thing also made the fall clear. The main factor of this pulverization is above TiCr<sub>2</sub>. It is presumed that it is an intergranular fracture on the basis of sludges, such as an intermetallic compound with A element. Therefore, if solidification speed becomes slow and the amount of such a sludge increases, the origin of pulverization will increase and pulverization will become easy to happen.

[0052] At the hydrogen storing metal alloy of the above knowledge to this invention, it is the main phase. (body center cubic) The diameter of average crystal grain is limited to 40 micrometers or less. Thereby, it is TiCr<sub>2</sub>. In order that the amount of generation of sludges, such as an intermetallic compound with A element, may decrease remarkably, hydrogen storage capacity increases and the alloy in which the high hydrogen storage capacity beyond H/M=1.80 approaching the maximum hydrogen storage capacity on the theory of a body center cubic metal is shown is obtained. MmNi<sub>5</sub> which the pulverization at the time of hydrogen absorption and discharge stops being able to happen easily repeatedly simultaneously, and is a typical rare earth system hydrogen storing metal alloy The endurance excellent more remarkably than a system intermetallic compound over hydrogen absorption and discharge comes to be shown repeatedly.

[0053] In order to improve further these properties of the hydrogen storing metal alloy of this invention, it is desirable that 20 micrometers or less of diameters of average crystal grain of the main phase are especially 15 micrometers or less. Moreover, TiCr<sub>2</sub> formed as the 2nd phase It was it hard coming to generate pulverization that the diameter of average crystal grain of sludges, such as an intermetallic compound with A element, was 5 micrometers or less, and it became clear to hardly carry out pulverization to it being 2 micrometers or less.

[0054] The diameter of average crystal grain of the main phase can manufacture the hydrogen storing metal alloy of this invention 40 micrometers or less by the rapid solidification method, as mentioned above. The method of concrete rapid solidification is not limited as long as an alloy with the above-mentioned diameter of average crystal grain is obtained. As an employable rapid solidification method, it is the method of carrying out teeming of the alloy molten metal on a rotational electrode process, a rotating drum, or a roll. (an example, a single roll, or congruence chill roll method) A method, the gas atomizing method, etc. which are thinly cast to up to a water-cooled copper plate are mentioned.

[0055] A rotational electrode process and the atomizing method have [ among these ] a powder configuration advantageous at the point that pack density becomes high in a globular form substantially, when the pulverization process for being able to manufacture the spherical-powder end of a hydrogen storing metal alloy, and powderizing becomes unnecessary. In the case of other methods, the hydrogen storing metal alloy obtained if needed is ground, and it is made powder. As the pulverization method, both hydrogenation pulverization and machine pulverization can be adopted and both may be used together.

[0056] It is appropriate for the hydrogen storing metal alloy of this invention to consider as the powder form whose mean particle diameter is about 10-50 micrometers. Thereby, a surface area increases and absorption and release reaction of hydrogen are promoted. If required, a classification will adjust a mean particle diameter.

[0057] The hydrogen storing metal alloy of this invention manufactured by the rapid solidification method has a minute quenching distortion. This quenching distortion is the endurance of the hydrogen storing metal alloy of this invention. (pulverization) Although not generated, especially a remarkable bad influence may heat-treat a hydrogen storing metal alloy by request, and may remove this quenching distortion. As for this heat treatment, it is desirable to carry out in a vacuum or inert gas in order to prevent oxidization of an alloy.

[0058] It is necessary to set up heat treatment conditions so that there may be no bird clapper during heat treatment more greatly [ the diameter of average crystal grain of the alloy main phase ] than 40 micrometers. This condition is usually temperature, although it changes also with diameters of average crystal grain of the main phase of the hydrogen storing metal alloy manufactured by the rapid solidification method. It is within the limits of 400-1000 degree-Cx 1 - 20 hours. However, when heat treatment temperature is as high as for example, more than 900 \*\*, heat treatment time is shortened and it is made for the diameter of average crystal grain of the alloy main phase after heat treatment not to exceed 40 micrometers. Since the heat treatment temperature of a Ti-V-Cr alloy is generally below 750 \*\*, the upper limit of heat treatment temperature can be made high by addition of B element.

[0059] When forming in an alloy front face nickel addition layer which makes a Ti-nickel compound a subject in order to raise the oxidation resistance of the hydrogen storing metal alloy of this invention so that it may mention later, it may heat-treat in the formation process of this layer, and quenching distortion is also removed during this heat treatment. Therefore, heat treatment of only the purpose of removal of the quenching distortion in that case is unnecessary.

[0060] The hydrogen storing metal alloy of this invention is the low temperature near the room temperature, when it is left in the atmosphere. (an example, 80 degrees C) The measured amount of hydrogen absorption may decrease. That is, if this alloy is left in the atmosphere, a front face will oxidize, and this oxide film is considered that it becomes an obstacle and the hydrogen storage capacity in low temperature decreases. Thus, the hydrogen storing metal alloy to which hydrogen storage capacity fell by air neglect is among high-pressure hydrogen gas. (an example, 20 atmospheric pressure) If you make it heated and activated to 500 \*\*, the amount of hydrogen absorption will increase and the amount of absorption before neglect will be recovered. However, as mentioned above, this activation requires costs.

[0061] It is desirable to improve the oxidation resistance of the hydrogen storing metal alloy of this invention so that it may not oxidize, even if it contacts the atmosphere, in order to avoid the above-mentioned activation with the equipment using the hydrogen storing metal alloy, since contact to the atmosphere is completely unavoidable in manufacture process.

[0062] As a result of examining this point, when the front face of the hydrogen storing metal alloy of this invention was covered with nickel like the publication to JP,60-190570,A, it became clear that the oxidation resistance of an alloy is improved. However, although this technique is effective in oxidation-resistant improvement, since the nickel itself which covered the alloy front face does not almost have hydrogen-absorption capacity, the amount of hydrogen absorption per alloy unit weight falls.

[0063] Then, when changed into nickel addition layer which nickel enveloping layer on the front face of an alloy is made to react with the Ti-V-Cr-A-B system alloy used as a base material as a result of inquiring further, and makes a Ti-nickel compound a subject, since this nickel addition layer has bigger hydrogen-absorption capacity than pure nickel, it turns out that oxidation resistance can be given to a hydrogen storing metal alloy, without reducing most amounts of hydrogen absorption. Therefore, in the suitable mode, the hydrogen storing metal alloy of this invention has nickel addition layer which makes a Ti-nickel compound a subject on the alloy front face. Oxidation resistance improves by that cause, without reducing hydrogen storage capacity substantially, and the activation mentioned above becomes unnecessary, or it is mitigated very much.

[0064] The covering method of nickel on the front face of an alloy is a physical method. (the method equivalent to the mechanical alloying mixed with an example, the method of mixing nickel impalpable powder and the end of an alloy powder, a ball mill, etc. is also included) Chemical method (an example, electrolysis nickel plating, non-electrolyzed nickel plating) Any are sufficient and there is especially no limit. Although the amount of covering of nickel changes also with powder mean particle diameters of a hydrogen storing metal alloy, 5 - 10 % of the weight is usually preferably suitable for it one to 20% of the weight to a hydrogen storing metal alloy. As long as it is required before this nickel covering, pickling processing of the hydrogen storing metal alloy may be carried out from the acid of non-oxidizing qualities, such as fluoric acid and a hydrochloric acid, and the oxidizing zone on the front face of an alloy may be removed.

[0065] After covering the front face of a hydrogen storing metal alloy with nickel, nickel addition layer which makes a Ti-nickel compound a subject is formed in a front face by heat-treating, making Ti component in a base material alloy nickel in surface coating react, and changing nickel layer to the high Ti-nickel compound of hydrogen-absorption capacity. Since this nickel addition layer has incorporated Cr from the base material, it excels the 2 yuan system intermetallic compound of Ti-nickel in oxidation resistance.

[0066] It is desirable to also perform this heat treatment in a vacuum or inert gas in order to prevent oxidization of an alloy. Heat treatment conditions are set up so that it will not change big and rough, by the time the diameter of average crystal grain of the main phase of a base material alloy exceeds 40 micrometers during this heat treatment.



This viewpoint to heat treatment temperature It considers as the range of 400-1000 degrees C, and heat treatment time is set up so that the above-mentioned big and rough-ization may not take place. If heat treatment temperature exceeds 1000 degrees C, big and rough-ization of the sludge of the 2nd phase progresses, and the amount of hydrogen absorption will fall or it will become easy to carry out pulverization of the diameter of average crystal grain to hydrogen absorption and discharge by the repeat. On the other hand, the generation reaction of a Ti-nickel compound cannot progress easily under by 400 \*\*. Desirable heat treatment temperature It is 450-900 \*\*.

[0067] However, it is a long time for example, in a ball mill about nickel covering. (an example and 100 - 1000 hours) Since it is nickel addition layer which generated nickel covering already reacts with Ti in a base material alloy, and makes a Ti-nickel compound a subject when it carries out by the mechanical alloying method for carrying out, it is not necessary to heat-treat for a reaction.

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[Translation done.]

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EXAMPLE

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[Example] In production of an examination alloy, it is a RF solution process. (5 kg/ch) Button arc solution process (button size : 250 g/ch and 50 g/ch) Single chill roll method which used the copper roll (20 g/ch) The Ar gas atomizing method (10 g/ch) Or rotational electrode process (500 g/ch) It used. The raw material used for manufacture of an alloy molten metal is a misch metal which is the alloy of a purity 99wt% titanium sponge, a purity 98wt% vanadium, purity 99wt% chromium, and a lanthanoids system rare earth metal. (It is written as Ln) It was purity 99wt% Fe, Mn, Co, Nb, Y, Zn and Zr, and purity 99.9wt% aluminum, Ag, Hf, Ta, W, Mo, and Cu (total La=46wt% and Ce=5wt% and Nd=37wt% and Pr=10wt% and rare earth content 99.5wt%). Light element (Si, C, N, P, B) Compound with Ti or Cr (TiC, TiB<sub>2</sub> grade) It added.

[0069] They are 300 \*\* and 2.5 MPa about the alloy obtained by methods other than the gas atomizing method powder is obtained directly, and a rotational electrode process. After hydrogenating in hydrogen gas for 5 hours, it ground mechanically, and it was made powder. Any end of an alloy powder is 100. The powder below mum was sorted out and used with the sieve. About a part of gas atomization material, in order to enlarge the diameter of average crystal grain, it heat-treated in argon atmosphere. The characterization method of an examination alloy is explained below collectively.

[0070] Hydrogen gas absorption, emission characteristic hydrogen gas absorption, and the emission characteristic were measured by the activation zero method using G BERUTSU type equipment. Measurement is 3.0MPa after putting in and carrying out evacuation of the examination alloy to a container and determining a zero. Under hydrogen pressure It carried out, after heating and carrying out activation to 300 - 500 \*\*. In order to remove the influence of oxidization of a front face in the end of an alloy powder in mechanical pulverization, it is a 5vol% hydrofluoric acid about an examination alloy before activation. (fluoric acid) Pickling was carried out in solution.

[0071] the hydrogen-desorption-absorption cycle used for measurement -- the temperature of 80 degrees C -- it is -- hydrogen pressure -- 3.0 MPa from -- the hydrogen gas discharge lowered to 0.01 MPa, and hydrogen pressure -- 0.01 MPa to 3.0 MPa up to -- it consists of hydrogen gas absorption to pressurize

[0072] Hydrogen storage capacity produces a hydrogen-desorption curve at the time of hydrogen gas discharge of 1 cycle eye, and is pressure 1MPa. The value of hydrogen storage capacity was calculated and it evaluated by converting this amount of hydrogen into H/M which is the ratio of the absorbed number of hydrogen atoms to the metal atomic number which constitutes an alloy. H/M considered 1.80 or more as success.

[0073] The influence of the pulverization by the pulverization repeat hydrogen absorption and discharge by repeat hydrogen absorption and discharge is the aforementioned hydrogen-desorption-absorption cycle 300 It measured and evaluated which powder with a particle size of 20 micrometers or less increased after cycle \*\*\*\*\*. The particle-size-distribution measuring device of a laser diffraction formula was used for the particle size analysis. Since the difference was in powdered particle size distribution by the manufacture method, evaluation computed the fines rate of increase compared to the amount on the basis of the particle weight 20 micrometers or less before an examination by the following formula, and evaluated it. It is success if the fines rate of increase is 15% or less.

[0074]

[Equation 1]

$$\text{微粉増加率(\%)} = \left[ \frac{A - B}{B} \right] \times 100$$

A=300 サイクル試験後の20μm以下の粉末量。  
B=試験前の20μm以下の粉末量。

[0075] After measurement of the diameter of crystal grain of the main phase of the diameter examination alloy of crystal grain embedded the alloy before pulverization at the epoxy resin and ground it, it \*\*\*\*\*ed by the

mixed acid of 0.4 vol% fluoric acid and a 1 vol% nitric acid, was observed with the optical microscope, and it was performed, and the average of the measurement result of 20 crystal grain chosen at random was made into the diameter of average crystal grain. Since it was detailed, the particle size of the sludge of the 2nd phase is SEM (secondary electron microscope). It used and measured and the average was calculated like the top.

[0076] Oxidation-resistant evaluation of the hydrogen storing metal alloy which carried out nickel covering of the oxidation-resistant front face, and formed nickel addition layer, the constant temperature of the temperature of 25 degrees C, and 65% of humidity -- G BERUTSU [ after leaving it for one week in the air atmosphere of constant humidity ] type hydrogen absorption / discharge testing device -- using -- activation -- nothing -- 80 degrees C -- 3.0 MPa The absorption test of hydrogen gas was performed and the decreasing rate of the hydrogen storage capacity in comparison with the hydrogen storage capacity of the alloy before forming nickel addition layer was computed by the following formula. It is success if the decreasing rate of hydrogen storage capacity is 10% or less.

[0077]

[Equation 2]

$$\text{水素吸収量低下率(\%)} = \left[ \frac{C-D}{C} \right] \times 100$$

C=Ni被覆前に活性化処理して測定した水素吸蔵量  
D=1週間放置後に70℃で測定した水素吸蔵量

[0078] (Example 1) this example is an example which alloy composition was changed and examined the performance of a hydrogen storing metal alloy. As a method of producing a hydrogen storing metal alloy, since only the rapid solidification method was adopted, each diameter of average crystal grain of the main phase was 40 micrometers or less, and many were 20 micrometers or less. The measurement result of the hydrogen storage capacity of each alloy and the fines rate of increase is shown in Table 1 with alloy composition and the producing method.

[0079]

[Table 1-1]

試験 No	化 学 組 成					溶解方法	水素 吸蔵量 (H/M)	微粉 増加率 (%)	備 考
	Ti	V	Cr	A	B				
1	0.30	0.37	0.30	Mn:0.02	Ln:0.01	ガスアライズ	1.81	8	本 発 明 例
2	0.30	0.29	0.30	Mn:0.10	Ln:0.01	"	1.84	9	
3	0.30	0.21	0.30	Mn:0.18	Ln:0.01	"	1.82	10	
4	0.30	0.37	0.30	Fe:0.02	Ln:0.01	"	1.81	9	
5	0.30	0.21	0.30	Fe:0.18	Ln:0.01	"	1.81	13	
6	0.30	0.37	0.30	Co:0.02	Ln:0.01	"	1.81	8	
7	0.30	0.21	0.30	Co:0.18	Ln:0.01	"	1.82	11	
8	0.30	0.37	0.30	Cu:0.02	Ln:0.01	"	1.81	10	
9	0.30	0.21	0.30	Cu:0.18	Ln:0.01	"	1.82	12	
10	0.30	0.37	0.30	Nb:0.02	Ln:0.01	"	1.82	8	
11	0.30	0.21	0.30	Nb:0.18	Ln:0.01	"	1.84	14	
12	0.30	0.37	0.30	Zr:0.02	Ln:0.01	"	1.81	8	
13	0.30	0.21	0.30	Zr:0.18	Ln:0.01	"	1.83	13	
14	0.30	0.37	0.30	Mo:0.02	Ln:0.01	"	1.81	9	
15	0.30	0.21	0.30	Mo:0.18	Ln:0.01	"	1.81	12	
16	0.30	0.37	0.30	Ta:0.02	Ln:0.01	"	1.82	8	
17	0.30	0.21	0.30	Ta:0.18	Ln:0.01	"	1.83	13	
18	0.30	0.37	0.30	Al:0.02	Ln:0.01	"	1.81	10	
19	0.30	0.21	0.30	Al:0.18	Ln:0.01	"	1.81	14	
20	0.30	0.37	0.30	Si:0.02	Ln:0.01	"	1.81	8	
22	0.30	0.21	0.30	Si:0.18	Ln:0.01	"	1.83	11	
23	0.30	0.29	0.30	Ag:0.10	Ln:0.01	"	1.82	8	
24	0.30	0.29	0.30	Hf:0.10	Ln:0.01	"	1.83	9	
25	0.30	0.29	0.30	W :0.10	Ln:0.01	"	1.81	12	
26	0.30	0.25	0.30	Mn:0.07 Fe:0.07	Ln:0.01	"	1.84	10	
27	0.30	0.25	0.30	Fe:0.07 Cu:0.07	Ln:0.01	"	1.84	11	
28	0.30	0.25	0.30	Co:0.07 Nb:0.07	Ln:0.01	"	1.85	11	
29	0.30	0.27	0.30	Mn:0.05 Hf:0.05 C :0.02	Ln:0.01	"	1.82	8	
30	0.30	0.27	0.30	Nb:0.05 W :0.05 N :0.02	Ln:0.01	"	1.83	9	
31	0.30	0.27	0.30	Zr:0.04 Si:0.04 P :0.04	Ln:0.01	"	1.82	11	
32	0.30	0.27	0.30	Zr:0.04 Mn:0.04 B :0.04	Ln:0.01	ガスアライズ	1.84	10	

[0080]

[Table 1-2]

試験 No.	化 学 組 成					溶解方法	水素 吸蔵量 (H/M)	微粉 増加率 (%)	考
	Ti	V	Cr	A	B				
33	0.30	0.24	0.30	Mn:0.05 Fe:0.05 Cu:0.05	Ln:0.01	"	1.88	10	本 発 明 例
34	0.30	0.24	0.30	Fe:0.05 Co:0.05 Nb:0.05	Ln:0.01	"	1.86	10	
35	0.30	0.256	0.30	Fe:0.14	Ln:0.004	"	1.81	9	
36	0.30	0.235	0.30	Fe:0.14	Ln:0.025	"	1.82	9	
37	0.30	0.25	0.30	Fe:0.14	Ln:0.01	"	1.83	8	
38	0.30	0.25	0.30	Fe:0.14	Ln:0.01	□-△ 急冷	1.83	8	
39	0.30	0.25	0.30	Fe:0.14	Ln:0.01	回転電極	1.83	10	
40	0.30	0.24	0.30	Fe:0.05 Co:0.05 Nb:0.05	Ln:0.01	□-△ 急冷	1.85	10	
41	0.30	0.24	0.30	Fe:0.05 Co:0.05 Nb:0.05	Ln:0.01	回転電極	1.85	12	
42	0.25	0.40	0.20	Fe:0.14	Ln:0.01	炉中冷却	1.81	8	例
43	0.48	0.10	0.38	Fe:0.03	Ln:0.01	"	1.84	13	
44	0.48	0.10	0.38	Fe:0.03	Y :0.01	"	1.85	11	
45	0.48	0.10	0.38	Fe:0.03	Ln:0.005 Y :0.005	"	1.85	10	
46	0.30	0.40	0.30	—	—	"	1.71	8	比 較 例
47	0.30	0.15	0.30	Mn:0.24	Ln:0.01	"	1.65	18	
48	0.30	0.15	0.30	Fe:0.24	Ln:0.01	"	1.52	20	
49	0.30	0.15	0.30	Co:0.24	Ln:0.01	"	1.55	17	
50	0.30	0.15	0.30	Cu:0.24	Ln:0.01	"	1.51	22	
51	0.30	0.15	0.30	Nb:0.24	Ln:0.01	"	1.45	18	
52	0.30	0.15	0.30	Mn:0.10 Fe:0.10 Cu:0.04	Ln:0.01	"	1.50	23	
53	0.30	0.15	0.30	Fe:0.10 Co:0.10 Nb:0.04	Ln:0.01	"	1.48	21	
54	0.30	0.225	0.30	Mn:0.14	Ln:0.035	"	1.66	8	
55	0.18	0.57	0.12	Fe:0.14	Ln:0.01	"	0.85	12	例
56	0.30	0.47	0.08	Fe:0.14	Ln:0.01	"	1.41	13	
57	0.60	0.13	0.12	Fe:0.14	Ln:0.01	"	1.52	20	
58	0.30	0.10	0.45	Fe:0.14	Ln:0.01	"	0.78	19	
59	0.30	0.16	0.30	Mn:0.24	—	"	1.76	18	
60	0.30	0.39	0.30	—	Ln:0.01	"	1.75	9	

[0081] As Table 1 shows, each hydrogen storing metal alloy whose alloy composition is within the limits of this invention is the comparatively low temperature near [ of 80 degrees C ] the room temperature, and is understood that H/M shows high hydrogen storage capacity called 1.80 or more, and the rate of pulverization by repeat hydrogen absorption / discharge examination is as low as 15% or less, and there is much hydrogen storage capacity also near the room temperature, and there is little degradation by repeat hydrogen absorption and discharge.

[0082] On the other hand, No.46 which did not add A and a B car element With the alloy, hydrogen storage capacity was low. No.59 which added only one element of A and B, and 60 Increase of hydrogen storage capacity was [ but ] inadequate. Simultaneously with the fall of hydrogen storage capacity, the rate of pulverization also increased with the alloy of No.47-53 which had too many additions of A element. No.54 which had too many additions of B element Hydrogen storage capacity fell with the alloy. Even when the addition of A and a B car element was suitable, when each of alloys of No.55-58 with the content of Ti, Cr, and V out of range [ this invention ] had low hydrogen storage capacity and there were too many Ti and amounts of Cr, the rate of pulverization became large.

[0083] (Example 2) this example is an example which considered the influence the diameter of average crystal grain of the main phase affects the performance of a hydrogen storing metal alloy about the hydrogen storing metal alloy from which the diameter of average crystal grain of the main phase produced by the various manufacture methods differs. The chemical composition of a hydrogen storing metal alloy is Ti=0.30, V= 0.24, Cr=0.30, A= 0.15 (Mn=0.04, Fe=0.03, Cu=0.03, aluminum=0.03, B= 0.05), and B= 0.01 (Ln=0.01). It considered as the same composition. In order to see the influence of the diameter of crystal grain, the examination alloy heat-treated after

gas atomization was also produced. A test result is shown in Table 2. [0084]

[Table 2]

試験 No.	溶 解 方 法	立方晶主相 の結晶粒径 ( $\mu\text{m}$ )	析出物の 結晶粒径 ( $\mu\text{m}$ )	水素 吸収量 (H/M)	微粉 増加率 (%)	備 考
1	ガスアトマイズ	16	0.8	1.86	10	本 発 明 例
2	ロール急冷	15	0.5	1.86	9	
3	回転電極	15	0.6	1.85	10	
4	ガスアトマイズ 熱処理: 680 °C×10hr	30	1.7	1.82	13	
5	ガスアトマイズ 熱処理: 950 °C×2 hr	35	2.1	1.84	15	
6	ボタンアーク溶解, 50g	48	4.5	1.60	21	比 較 例
7	ボタンアーク溶解, 250g	70	9.5	1.55	25	
8	高周波溶解, 5 kg	85	10.6	1.25	32	
9	ガスアトマイズ 熱処理: 900 °C×15hr	45	4.2	1.55	20	
10	ガスアトマイズ 熱処理: 1300°C×10hr	65	5.5	1.40	33	

[0085] If a hydrogen storing metal alloy is produced by the rapid solidification method as shown in Table 2, the alloy of a detailed organization 20 micrometers or less will be obtained for the diameter of average crystal grain of the main phase. Although the diameter of crystal grain became big and rough when the hydrogen storing metal alloy of this detailed organization was heat-treated, when the diameter of average crystal grain of the main phase was 40 micrometers or less, both the amount of hydrogen absorption and the fines rate of increase were success. About the diameter of average crystal grain, if it is 40 micrometers or less, there will be no bad influence to the hydrogen storage capacity and the fines rate of increase by heat treatment also at the hot heat treatment in the alloy of this invention 950 \*\* for a short time. However, the direction of an alloy 20 micrometers or less had the high-achieving diameter of average crystal grain which has not been heat-treated after rapid solidification, and the fines rate of increase became 10% or less the top where hydrogen storage capacity is also high.

[0086] Moreover, the desirable range of the suppression of pulverization especially of [ that the diameter of average crystal grain of the main phase is 40 micrometers or less ] 2 micrometers or less also understands 5 micrometers or less also of diameters of average crystal grain of the sludge of the 2nd phase to be also a bird clapper from Table 2.

[0087] On the other hand, as for the late button arc dissolution material and late RF dissolution material of solidification speed, the diameter of average crystal grain of the main phase exceeded 40 micrometers, and both hydrogen storage capacity and the fines rate of increase became a rejection. (No.6-8) . When gas atomization material was heat-treated and heat treatment conditions were set up so that the diameter of average crystal grain might exceed 40 micrometers, hydrogen storage capacity and the fines rate of increase both fell greatly too (No.9, 10).

[0088] (Example 3) this example illustrates the oxidation-resistant improvement in the hydrogen storing metal alloy at the time of forming in an alloy front face nickel addition layer which makes a Ti-nickel compound a subject. Each examined hydrogen storing metal alloy is the powder produced by the Ar gas atomizing method. The chemical composition of an alloy was taken as the same composition of Ti=0.30, V= 0.25, Cr=0.30, A= 0.14, and B= 0.01. (however, the element kind of A and B change) .

[0089] nickel covering of the hydrogen storing metal alloy powder for forming nickel addition layer adopted both the physical method and the chemical method. By the physical method, after blending this 10% of the weight to the end of an alloy powder using nickel impalpable powder with a particle size of about 1 micrometer, it mixed uniformly with the mortar or mixed with the ball mill for a long time. The chemical method formed about 10% of the weight of nickel plating layer in the front face in the end of an alloy powder using commercial non-electrolyzed nickel plating liquid. In addition, though natural, even if it performs electrolysis plating, same nickel plating layer can be formed.

[0090] After giving nickel covering by these methods, nickel addition layer which makes a Ti-nickel compound a subject was formed in the alloy front face by heat-treating in argon atmosphere, making nickel enveloping layer react with the end of an alloy powder, and alloying. However, with the method of covering nickel powder with a ball mill mechanically, it is this ball mill mixture 100 Since alloying of nickel covering by mechanical alloying had taken place by carrying out time and for a long time, heat treatment was not performed. Moreover, as an example of comparison, this heat treatment is not performed but it is only nickel covering. (non-electrolyzed nickel plating or mortar mixture) The test coupon carried out was also produced.

[0091] In this way, it investigated by measuring hydrogen storage capacity, without carrying out activation of the oxidation resistance of the hydrogen storing metal alloy powder produced by the gas atomizing method for having formed nickel content layer on the front face after the neglect for one week in the atmosphere of predetermined conditions as mentioned above. About a test result, it is the formation method of nickel addition layer. (an upper case is the nickel covering method and the lower berth is heat treatment conditions) Existence of formation of the diameter of average crystal grain of the main phase, and a Ti-nickel compound phase (it checks by the X diffraction) It is shown in Table 3.

[0092]

[Table 3]

試験 No.	化学組成 <sup>1)</sup>		作製方法	Ni含有相形成 上: Ni付着法 下: 熱処理	平均 結晶 粒径	Ti-Ni 化合物 相形成	吸蔵量 低下率 (%)	備 考
	A	B						
1	Mn:0.07 Fe:0.07	Ln:0.01	ガスアライズ	無電解めっき 680℃×10hr	27 $\mu$ m	有	7	本 発 明 例
2	Mn:0.07 Fe:0.07	Ln:0.01	"	Ni粉末混合 680℃×10hr	27 $\mu$ m	有	10	
3	Mn:0.07 Fe:0.07	Ln:0.01	"	Ni粉末混合 680℃×10hr	15 $\mu$ m	有	9	
4	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき 400℃×10hr	20 $\mu$ m	有	6	
5	Co:0.07 Nb:0.07	Y :0.01	"	無電解めっき 680℃×25hr	23 $\mu$ m	有	5	
6	Zr:0.07 Ta:0.07	Y :0.01	"	無電解めっき 680℃×25hr	32 $\mu$ m	有	9	
7	Fe:0.04 Ta:0.04 Al:0.03 Si:0.03	Ln:0.01	"	無電解めっき 680℃×10hr	25 $\mu$ m	有	7	
8	Mn:0.04 Al:0.04 C :0.03 B :0.03	Ln:0.01	"	無電解めっき 680℃×10hr	23 $\mu$ m	有	8	
9	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき 950℃×2 hr	33 $\mu$ m	有	7	比 較 例
10	Mn:0.07 Fe:0.07	Ln:0.01	ガスアライズ	なし	15 $\mu$ m	—	35	
11	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき	15 $\mu$ m	無	19	
12	Mn:0.07 Fe:0.07	Ln:0.01	"	Ni微粉末混合	15 $\mu$ m	無	24	
13	Mn:0.07 Fe:0.07	Ln:0.01	"	無電解めっき 900℃×10hr	42 $\mu$ m	有	22	

<sup>1)</sup> Ti=0.30、V=0.25、Cr=0.30、A=0.14、B=0.01

[0093] As shown in Table 3, nickel covering was given according to this invention, when nickel addition layer which makes a Ti-nickel compound a subject by making nickel covering of a parenthesis react with an alloy content was formed in the alloy front face, oxidization in the atmosphere of the hydrogen storing metal alloy of this invention was suppressed, and even if it measured hydrogen storage capacity, without carrying out activation after one-week neglect, the fall of hydrogen storage capacity was suppressed to 10% or less. That is, since a front face hardly oxidizes even if it deals with the powder of a hydrogen storing metal alloy in the atmosphere, the activation which handling becomes very easy and costs require does not have needlessness, and is mitigated.

[0094] On the other hand, in the example of comparison, when nickel covering was not given at all, the amount of hydrogen absorption of the alloy-powder end after one-week neglect fell no less than 35% (No.9). However, even if it gave nickel covering, when nickel covering was not made to react with an alloy content by heat treatment or mechanical alloying, the amount of hydrogen absorption of the alloy-powder end after one-week neglect fell no less than 19 to 24%. (No.10, 11). That is, compared with the case of not covering, it turns out only by nickel covering that oxidation-resistant improvement is remarkably few. Moreover, when the heat treatment conditions for the reaction after nickel covering were unsuitable and the diameter of average crystal grain of the main phase exceeded 40 micrometers, hydrogen storage capacity fell greatly too under the influence of big-and-rough-izing.

[Translation done.]